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THE DECOMPOSITION OF CRYSTALLINE SODIUM AZIDE BY X RAYS[1]

BY H. G. HEAL[2]

ABSTRACT

Sodium azide is decomposed by X rays. The yields of nitrogen gas, ammonia, and hydroxyl ion obtained when irradiated crystals are dissolved in water are proportional to total dose and independent of dose rate, for small amounts of decomposition. The yields per unit dose at 102° are 1.3 times those at 51°. The nature of the decomposition products in the crystals is uncertain, but the absorption spectrum seems to rule out the formation of sodium. A mechanism for the decomposition is suggested.

INTRODUCTION

The decomposition of solid azides by heat and by ultraviolet light, as well as the chemiluminescence accompanying the thermal decomposition, have been investigated in some detail. Apart, however, from a very few observations on barium azide (6), little is known of the decomposition of solid azides by ionizing radiation. The alkali metal azides form an attractive point of entry into the little explored field of radiation-induced reactions in solids. Among the reasons for this are the fact that their heats of formation are approximately zero, which makes it unlikely that decomposition will be thermally propagated at ordinary temperatures from points where it is initiated by radiation, and the general similarity of their structure to that of the alkali halides, the behavior of which under irradiation is beginning to be well understood.

The objectives of the present investigation were:

(*a*) To determine, as far as possible, the chemical nature of the products formed in solid sodium azide by X irradiation, using a combination of chemical analysis and spectrophotometry.

(*b*) To study the variation of yields with total dose, dose rate, and temperature, in the hope of arriving at a mechanism for the decomposition.

EXPERIMENTAL

Preparation of Materials

B.D.H. sodium azide was recrystallized once by allowing a solution saturated at about 70°, and filtered, to cool to room temperature. The product was

[1] *Manuscript received June 23, 1953.*
Contribution from the Chemistry Department, University College of the West Indies, Mona, St. Andrew, Jamaica, B.W.I.

[2] *Present address, Queen's University, Belfast, Northern Ireland.*

filtered. The crystals were washed successively with pure ethanol and pure acetone, air-dried, and stored in a desiccator.

Analysis of Starting Material

Samples of about 0.1 gm. of the recrystallized azide were dissolved in an excess of pure 1*N* hydrochloric acid, and the solution evaporated to dryness under an infrared lamp. The residue was moistened with more hydrochloric acid, again dried under the lamp, and weighed. The weight ratio NaCl: NaN_3 should be 0.899. Values found were 0.893, 0.909.

Irradiation Arrangements

Irradiations were carried out by means of a Siemens "Dermopan" skin therapy unit. This has a beryllium-windowed X-ray tube operating at 50 KVP and 25 ma. maximum. The tube is supplied with unrectified alternating high voltage. All irradiations were performed at 50 KVP.

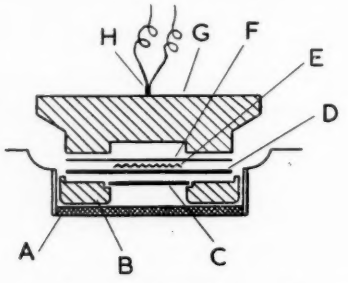

FIG. 1. Vertical section through sample holder (one and two-thirds times actual size).

The sample holder is shown in Fig. 1. A circular brass ring *B* rests directly on the window *A* of the X-ray tube. *C* is an aluminum disk, the thickness of which can be selected to provide the desired degree of filtration. *D* is a disk of 0.08 mm. aluminum foil, on which the sample *E* rests. *F* is a disk of 0.04 mm. aluminum foil, placed over the sample. The whole arrangement is weighted down by means of the brass block *G*, which presses the foil disks *D* and *F* firmly down on the ring *B* around their periphery. The sample is thus enclosed in a lens-shaped cavity, and is entirely surrounded by aluminum. *H* is a copper-constantan thermocouple junction soldered to *G*.

Very small samples were used in order to take advantage of the intense radiation field existing close to the window of the X-ray tube. By keeping the samples thin, it was possible to irradiate them uniformly with quite soft X radiation, so that the amount of filtration could be kept to a minimum, and the intensity correspondingly increased. Samples were irradiated for periods ranging from half an hour to five hours. The largest amount of decomposition achieved was approximately 2.5%.

Irradiation Procedure

The sodium azide consisted largely of platelets 1–3 $mm.^2$ in area and 0.05–0.1 mm. thick. A few milligrams of these were spread out on black paper.

For each irradiation, approximately 2 mgm. of platelets free from thick places were selected by means of a small glass probe, and spread out over the central area of disk *D* (Fig. 1) in such a way that no two platelets overlapped.

The current and voltage were manually controlled in all irradiations.

The heat generated by the X-ray tube in normal operation was allowed to determine the sample temperature. Two different temperatures (51° and 102°) were obtained by operating the tube with 8.3 ma. and 25 ma. current respectively. One hundred and two degrees is far below the temperature at which sodium azide begins to decompose thermally (4). Two to three minutes' operation were required before the temperature became steady. Since none of the irradiations done in the course of the chemical work lasted less than thirty minutes continuously, and the temperature coefficient of the decomposition rate is not large, it was not necessary to correct for the short period during which full operating temperature had not been reached. The room temperature, which, of course, partly determined the sample temperature, was always within ±2° of 28°. It is unlikely that the sample temperatures deviated more than ±3° from the figures given above.

The effect of intensity upon the decomposition rate, at constant temperature, was determined by changing the thickness of the filter *C*, which enabled the rate of energy absorption in the sample to be varied by a factor up to 3.5. The highest intensities at 51° overlapped with the lowest intensities at 102°, so that the decomposition rates at the two temperatures could be compared for equal intensities. The relative intensities for different filter thicknesses were calculated, using De Waard's formula (3) for the spectral energy distribution, and tabulated values for the mass absorption coefficients of beryllium, aluminum, sodium, and nitrogen (7). Characteristic lines in the spectrum were neglected. If, as is almost certainly the case,* the target is tungsten, the only such lines concerned are the *L*-lines, which fall at wave lengths near the middle of the spectrum of radiation absorbed by the salt, so that their intensity would vary with filtration in roughly the same way as that of the 'white' radiation. In any case, the integrated intensity in the characteristic lines should be small compared with that of the 'white' radiation.

Sodium azide does not deliquesce unless the relative humidity is very high. All irradiations were performed during the dry season, and at temperatures of 51° or 102°. The salt therefore remained perfectly dry, and there was no visible corrosion of the aluminum foil where it had touched the crystals, even after many irradiations.

Analysis of Samples

The volume of gas evolved when the sample dissolved in water, and the amounts of hydroxyl ion and ammonia in the resulting solution, were determined.

The method of gas analysis has been described in a recent Note (8). Rather than weigh the samples, it was found convenient to determine the amount of

**No information on this point could be obtained.*

azide in them colorimetrically. The solution from the gas determination was washed into a 25 ml. volumetric flask. To it were added 2.5 ml. of a solution containing 10 gm. A.R. ferric ammonium sulphate and 10 ml. of 3*N* sulphuric acid per liter. The solution was diluted to 25 ml. and its transmission measured by means of an EEL photoelectric colorimeter, with blue filter. The ferric azide color was found to be stable for the few minutes required for transmission measurements.

Attempts to determine hydroxyl ion and ammonia by titration with a microburette were abandoned after a few trials. It was not practicable to titrate the hydroxyl ion from 2 mgm. samples in a volume greater than about 0.2 ml., and such small volumes were difficult to protect adequately from atmospheric carbon dioxide during a titration. Moreover, the ammonia present spoiled the end point, and was partly lost by volatilization during the time required for a titration, so that it could not easily be corrected for. Nevertheless, the results obtained for both hydroxyl ion and ammonia by titration methods agreed substantially with those given by the methods now to be described.

Hydroxyl Ion was determined colorimetrically. In these determinations it was necessary to keep the solutions decidedly alkaline throughout, in order to prevent hydrolysis of the undecomposed sodium azide. The sample was added to a solution of phenolphthalein containing about half the indicator in the acid form and half in the alkaline form. The number of equivalents of phenolphthalein present was made much greater than the number of equivalents of hydroxyl ion given by the sample. Under these conditions it can be shown that the change in concentration of the pink alkaline form is approximately a linear function of the quantity of hydroxyl ion added. Experimentally, two eight-milliliter portions of a nearly saturated aqueous phenolphthalein solution were placed in matched colorimeter tubes, each of which contained a thin glass stirrer so contrived as not to interfere with the passage of the light beam in the colorimeter. Decinormal baryta (0.01 ml.) was added to each tube from a micropipette. The purpose of this was to convert nearly half the indicator to the alkaline form, and at the same time to remove dissolved carbon dioxide as barium carbonate. The solutions were stirred, left to stand five minutes, stirred again, and measured in the colorimeter with green filter, using tube 1 as a blank with which tube 2 was compared. The azide sample, about 2 mgm. of the irradiated salt, was then added to tube 2. The contents of both tubes were stirred simultaneously and in the same manner, after which the transmission of tube 2 was again compared with that of tube 1. The identical treatment of the two ensured that atmospheric carbon dioxide picked up during the operations could not affect the result, which depended, to a first approximation, only on the *difference* between the transmissions of the two tubes. The method was calibrated by means of known amounts of standard baryta. It proved to be quite convenient for the determination of amounts of hydroxyl ion up to about 0.6 microequivalent. Since the concentrations of acid and alkaline forms of the indicator were never far from equality, the pH of the solutions must always have been close to pK for phenolphthalein,

which is 9.6. This made it possible to correct satisfactorily for the hydroxyl ion formed from ammonia in the solution by the reaction.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

for it follows from the equilibrium constant for this reaction that one third of the total ammonia present in solutions of pH 9.6 is in the form of NH_4^+ and the rest as NH_3. On account of the comparatively large volume of solution, no appreciable amount of ammonia could be lost during measurements (2).

The unirradiated azide gave a very small quantity of hydroxyl ion, for which all results were corrected.

After measurement of the optical transmission of the phenolphthalein solution containing the irradiated azide, the quantity of azide in the solution was found simply by adding the ferric sulphate reagent and measuring the transmission of the ferric azide with a blue filter. The color of the phenolphthalein was, of course, discharged by the acid in the reagent, and so did not interfere.

The quantities of *ammonia* given by the samples never exceeded 0.3 microequivalent. The irradiated samples were dissolved in 0.2 ml. water, 0.02 ml. Nessler's reagent added, and the precipitates compared with those given by a series of standards made up with unirradiated sodium azide and known amounts of ammonium chloride, all in small matched test tubes.

Like ammonia, hydrazine gives a brown precipitate with Nessler's reagent. Hydroxylamine, the only other likely reaction product, gives on the other hand a grey precipitate. The following tests showed that a little hydrazine was present in the solutions of irradiated azide, but that nearly all the precipitate with Nessler's reagent was due to ammonia. A sample of sodium azide irradiated sufficiently to decompose about 2% of it was dissolved in 0.1 ml. water. Comparison samples containing the same weight of unirradiated sodium azide in the same volume, and in addition known amounts of hydrazine, were also prepared. Ammoniacal silver nitrate solution (0.1 ml.) was added to each. The irradiated sample gave a scarcely visible stain of silver on the walls of the tube. By visual comparison with the standards, the number of moles of hydrazine responsible for this was estimated. This quantity, when added to Nessler's reagent in the presence of 2 mgm. of unirradiated sodium azide, gave only a faint yellow coloration, in place of the substantial brown precipitate given by a sodium azide sample, which had been irradiated with the same dose as previously. The number of moles of hydrazine formed was not more than about one-sixth the number of moles of ammonia. The coloration given with Nessler's reagent by the hydrazine alone was not strong enough to justify any attempt to correct for it, and it was ignored in the ammonia determinations.

Measurement of Spectra

A Unicam quartz spectrophotometer was employed.

RESULTS AND DISCUSSION

General

The sodium azide turned brown when irradiated. The color of thin crystals about 0.3% decomposed was scarcely visible. Samples 2.5% decomposed

were dark in color, but still transparent in a thickness of 0.1 mm. Under the microscope, with 50 diameters magnification, the color appeared uniform, and no nuclei were seen.

Irradiated samples dissolved in water with effervescence, forming a mist of fine gas bubbles. The speed of dissolution increased with the dose received. It was very fast for samples 2.5% decomposed. If, however, samples which had been irradiated at 51° were heated for several hours at 100° before dissolving, they dissolved very much more slowly than crystals similarly irradiated and not heated. The total volume of gas evolved was slightly increased by the heating.

The evolution of gas during dissolution continued steadily from each crystal until the last minute particle had dissolved. This shows that the decomposition took place throughout the bulk of the material, and was not confined to external surfaces or their immediate neighborhood.

The Chemical Data

These are plotted in Figs. 2 and 3. The energy values on the abscissae were not measured, but have been calculated from figures for the roentgen intensity of radiation from the "Dermopan" given by Graul (5). Graul's values are only for intensities 5 cm. and 10 cm. from the target. The azide samples were irradiated at 1.45 cm. from the target. The intensity at this distance was taken to be the mean of values calculated from the intensities at 5 cm. and 10 cm. by applying the inverse square law. This, of course, is only a rough estimate, and an error of ±25% is certainly possible. The *relative* energy absorptions for the different experimental points in Figs. 2 and 3, however, are correct within ±5%.

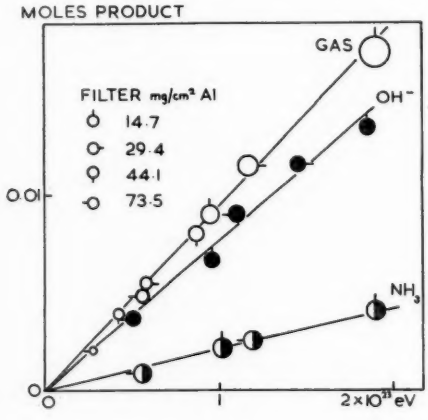

FIG. 2. Dependence of yields of gas, hydroxyl ion, and ammonia, per mole azide, upon X-ray energy absorbed per mole, at 51°. (Radii of circles represent estimated probable analytical errors.)

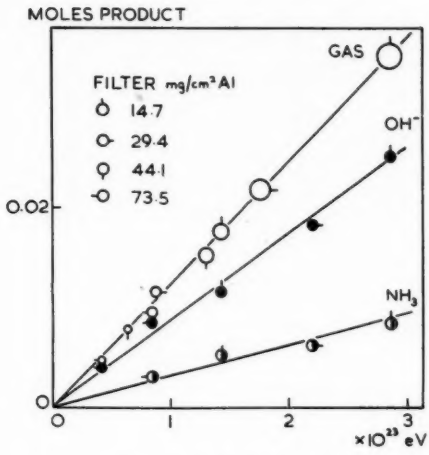

FIG. 3. As Fig. 2, but at 102°.

The Influence of Total Dose and Dose Rate on the Yield

At 51° and 102° the yields of gas, hydroxyl ion, and ammonia all seem to be proportional to the total dose. This conclusion can be stated with less confidence for the ammonia yields than for the others, on account of the large experimental error in this case. The points for all filters lie on or near the same straight lines. Hence the yield for a given dose is practically independent of the dose rate, over the ranges of dose rates studied. The dose rates at 51° ranged from 0.28×10^{23} ev./mole/hr. to 0.96×10^{23} ev./mole/hr. Those at 102° ranged from 0.85×10^{23} ev./mole/hr. to 2.87×10^{23} ev./mole/hr.

In view of this behavior, and since the gas determinations in particular are easily carried out, sodium azide seems worthy of further study as a chemical dosimeter for intense radiation fields.

The G' value (1) (number of molecules of sodium azide decomposed per estimated 100 ev. absorbed) is 5.2 at 102° and 4.0 at 51°. The possible error in these values is of the order of 1.0, but cannot be estimated accurately.

The Influence of Temperature

For a given dose rate, the rates of formation at 102° of the three products analyzed for averaged 1.3 times the corresponding rates at 51°. This corresponds to a thermal activation energy of 500 cal./mole.

Significance of the Chemical Data

The yields of gas, hydroxyl ion, and ammonia were in the ratio 1 : 0.81 : 0.22 at 51°, and in the ratio 1 : 0.72 : 0.25 at 102°.

At least two simple modes of decomposition could give these values. The ammonia in the aqueous solution might have come from nitride ion formed in the reaction

$$3\ N_3^- \rightarrow N^{3-} + 4\ N_2$$

followed by

$$N^{3-} + 3\,H_2O \rightarrow NH_3 + 3\,OH^-,$$

which would give four moles nitrogen : three equivalents hydroxyl ion : one mole ammonia, assuming no nitrogen to be lost during irradiation. The experimental ratios are 4 : 3 : 1 within the error of measurement.

Alternatively, the ammonia may have been formed through the reduction of azide ion in solution by the hydrogen atoms formed when free electrons or minute aggregates of sodium metal come in contact with water.

$$Na + H_2O \rightarrow Na^+ + OH^- + H$$

or

$$e + H_2O \rightarrow OH^- + H.$$

Since the concentration of azide ions in the solution next to the dissolving crystal surface is so much higher at all times than that of hydrogen atoms, reduction of azide ion to ammonia may well occur much more often than the union of hydrogen atoms to hydrogen molecules. If, then, the reaction occurring under irradiation were

$$NaN_3 \rightarrow Na + 3/2\,N_2$$

and the sodium were fairly efficiently utilized in reducing azide ion to ammonia during dissolution, the relative yields of gas, hydroxyl ion, and ammonia would, as is easily shown, be the same as in the case of the previously postulated mechanism. Thus the chemical data alone provide no way of distinguishing between these two mechanisms. Still others can be imagined (such as the formation of N^{2-} or N^- in the crystals) which would probably lead to the same result in solution. It would evidently be very difficult to find purely chemical methods of discriminating between these alternatives. An independent line of evidence was sought in the study of absorption spectra of the irradiated crystals.

The chemical data prove:

(*a*) That the gas evolved on dissolution must have been practically pure nitrogen (since, with the observed ratio of hydroxyl ion to ammonia, little free hydrogen can have been formed).

(*b*) That little or no gas can have escaped from the crystals during irradiation (since all the nitrogen which could have been formed, in conjunction with the hydroxyl ion and ammonia found, was actually recovered on dissolution).*

The Absorption Spectrum

Spectra were measured for several different samples. Fig. 4 shows one set. The spectra are those of a crystal plate of mean thickness 0.13 mm., but rather irregular, the thickest places being about 0.2 mm. thick and the thinnest about 0.1 mm. It was irradiated 15 min. at 51°. 0.18% of the material was decomposed. Spectrum A was plotted immediately after irradiation. Spectrum B is that of the same sample after 18 hr. storage in the dark. The height of the peak at 3400 Å has diminished slightly. Spectrum C is that of the same sample

*Storage after *irradiation for periods up to 48 hr. was found to have no measurable effect on the volume of gas recovered. All samples were analyzed within 48 hr. of irradiation, and nearly all within 24 hr.*

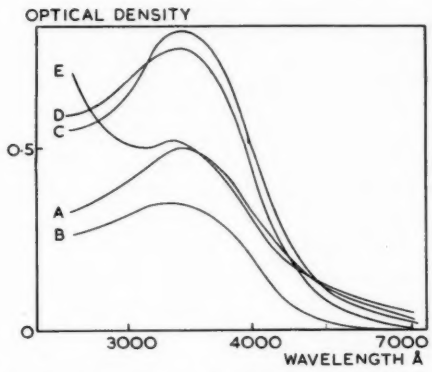

FIG. 4. Absorption spectra of irradiated sodium azide plate. (The optical densities are relative to those of the same crystal before irradiation.)

immediately after a further 15 min. irradiation, i.e. about 0.36% decomposed. Spectrum D is the same after 24 hr. storage in darkness. Again the 3400 Å peak has declined somewhat. Spectrum E was obtained after this sample had been heated 24 hr. at 100°. Here a big decline in the 3400 Å peak is in evidence.

The 3400 Å peak was the only one observed in the spectra of irradiated sodium azide crystals, between 2800 Å, where the absorption of sodium azide itself begins, and 7000 Å.

On account of the small transmission near this peak, and the irregular thickness of the crystal, these spectra are not to be relied upon in detail, but there is no doubt of the position and qualitative height changes of the absorption band, which were similar for several specimens which were similarly treated.

The band with the peak at 3400 Å probably does not arise from F centers, for the following reason. Simpson (10), and others have obtained good results for the energy of the $1s \rightarrow 2p$ optical transition in the F centers of sodium chloride, by calculations in which the only parameters required were the lattice spacing and the static and dynamic dielectric constants of the crystal. Now the azide ion is intermediate in volume between the bromide ion and the iodide ion. Hence it must be roughly as polarizable as these ions. The static and dynamic dielectric constants of sodium azide cannot, therefore, be very different from those of sodium bromide and iodide, and its lattice spacing is intermediate between those of the bromide and iodide. It is therefore unlikely that the absorption band of F centers in sodium azide can lie very far away from those of similar centers in the bromide and iodide, which occur at 5400 Å and 5880 Å respectively. Actually the 3400 Å band in irradiated sodium azide approaches in position the F band in lithium fluoride (2570 Å), the ions of which are very much smaller and less easily polarized than those of sodium azide. It is reasonable to conclude that the 3400 Å band is not an F band, (i.e. that it is not due to electrons trapped in anion vacancies). However, the *total absence* of an F band in the expected position is hard to explain. One would

expect some F centers to be formed, even if they are not the principal product of irradiation. This suggests that some important factor may have been left out of account in the argument just given.

The band at 3400 Å is not nearly intense enough to be accounted for by an allowed transition in one of the major reaction products. If the absorption in this band is due to a major product, the oscillator strength for the transition, calculated by the formula of Smakula (11) is only 0.04 approximately. The changes in height of the peak on standing and on heating are not accompanied by any corresponding changes in the chemical gas yield. It seems more likely, therefore, that this band is due to absorption in a minor reaction product not identified, than that it is caused by a forbidden transition in a major product.

One reasonably certain conclusion from the absorption spectra is that the irradiated crystals do not contain colloidal sodium metal, which would give a broad band in the visible.

A Possible Mechanism

Jacobs and Tompkins (9) found that potassium azide is decomposed by ultraviolet light via a mechanism involving the reaction of two excitons, which leads to a decomposition rate proportional to the square of the radiation intensity. The rate of decomposition of sodium azide by X rays, however, is proportional to the first power of the intensity. The simplest possible mechanism consistent with this fact, and with the chemical and spectroscopic evidence as to the nature of the products, would be the dissociation of excited azide ions according to the equation

$$N_3^- \rightarrow N^- + N_2$$

at lattice imperfections of various kinds. The excitons would have to be at a higher level of excitation than those produced in the ultraviolet decomposition. The fraction of X-ray excited azide ions actually decomposing cannot be much less than 0.25 here* (in contrast with the value of 0.001 for the ultraviolet photolysis of KN_3) so that mechanisms requiring the interaction of two excitons seem less likely than single-exciton mechanisms.

There is no obvious reason why an assembly of Na^+ and N^- ions should not be stable.

When the crystals dissolve, the following sequence of reactions may take place:

$$\begin{aligned}
N^- &+ H_2O \rightarrow NH + OH^- \\
NH &+ N_3^- \rightarrow NH^- + 3/2\ N_2 \\
NH^- &+ H_2O \rightarrow NH_2 + OH^- \\
NH_2 &+ N_3^- \rightarrow NH_2^- + 3/2\ N_2 \\
NH_2^- &+ H_2O \rightarrow NH_3 + OH^-
\end{aligned}$$

which would give the observed chemical products in the proper ratio. This mechanism also accounts for the trace of hydrazine found in the solutions, which could be formed by combination of pairs of NH_2 or NH radicals.

**Since the energy required to excite an azide ion is at least 5 ev., and only about 20 ev. are consumed per azide ion decomposed.*

The very low thermal activation energy (500 cal/mole), deduced from the temperature coefficient of the decomposition rate, is consistent with the observed high probability of dissociation of excited azide ions.

ACKNOWLEDGMENT

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IRRADIATION OF ONE MOLAR AQUEOUS CHLORAL HYDRATE SOLUTION WITH Co^{60}-GAMMA-RAYS AND BETATRON X RAYS[1]

By G. R. Freeman, A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

The production of acid by irradiation of 1 *M* chloral hydrate solutions is proportional to the dose at a given dose rate. The specific yield is the same for Co^{60} γ-rays as for 23 Mev. peak energy X rays and is a linear function of the inverse of the square root of the dose rate. The reaction is apparently a chain reaction.

INTRODUCTION

Many organic halogen compounds liberate the corresponding halogen acid when irradiated in aqueous systems and in some cases the radiation yield is quite high. Since it is relatively easy to analyze for strong acids by a variety of methods, it has been suggested that such systems might be useful as chemical radiation dosimeters or actinometers.

In addition to having a yield that is high, an acceptable dosimeter should have a yield that is, (i) zero order with respect to the concentration of the substance undergoing chemical change, (ii) independent of intensity over a wide intensity range, (iii) independent of the energy of the radiation, (iv) not too dependent on temperature, and (v) not too dependent on traces of impurities, rigorous purification of reagents, etc.

Andrews and Shore (1) studied the aqueous chloral hydrate system using 50–200 kv. X rays, and dose rates from 9 to 360 kr./hr. They found that the chief ionizable product formed was hydrochloric acid, and that a smaller amount of a weakly ionized acid was also probably formed. They found that the radiation yield was dependent on chloral hydrate concentration and on temperature, and was independent of dose rate over the range investigated.

In the present experiments the effects of photon energy and dose rate were studied using aerated one molar aqueous solutions of chloral hydrate. The dose rate was in general lower than that used by Andrews and Shore.

MATERIALS AND METHODS

The water used in the chloral hydrate solutions was distilled from alkaline potassium permanganate, then from an alkaline suspension of manganous hydroxide, and finally from a Pyrex still equipped with a quartz condenser and a quartz receiving flask.

May and Baker's reagent grade chloral hydrate was used without further purification. Since an induction period was observed in the radiation reaction with solutions that were about four days old, the reported results were obtained using solutions which were never more than 36 hr. old.

Solutions were irradiated in Pyrex test tubes with ground-glass stoppers. These tubes were cleaned with hot chromic acid cleaning solution, rinsed repeatedly with tap water and then six times with the specially distilled water.

[1] *Manuscript received July 13, 1953.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

A microburette consisting of a glass siringe and a micrometer screw (6), on which one unit corresponded to 1.5×10^{-4} ml., was used to titrate the acid produced with 0.01 *N* sodium hydroxide. Bromcresol purple indicator was used, each irradiated solution being titrated to the color shade shown by a blank. The indicator solution was prepared according to the directions of Kolthoff and Rosenblum (7) with the pH adjusted to 3.5.

One molar chloral hydrate solutions were used in all experiments. Filtration of the solutions through glass wool did not affect the yield of acid.

Irradiations of the chloral hydrate solutions were carried out using $Co^{60}\gamma$-ray sources of 1.2 curies and 1100 curies respectively and X rays from a betatron. In order to offset any fluctuations and lack of homogeneity in the betatron X-ray beam, the samples were placed in a rotating cylindrical lucite block. (For experimental details, see (3) and (5).)

The dose rate was determined using a Victoreen Condenser r.-meter Model 70 and the usual corrections were applied for energy, temperature, and pressure (5). The energy correction factors for X rays from the betatron were calculated. They were 1.06 and 1.08 for 15 and 22 Mev. peak energies, respectively (3).

EXPERIMENTAL RESULTS

Irradiation with Co^{60} γ-Rays

The effect of variations in temperature on specific yield of acid is shown in Table I. Since the system had a temperature coefficient of 2.5% per degree

TABLE I
VARIATION OF SPECIFIC YIELD OF ACID WITH TEMPERATURE

Temp., °C.	Dose rate (kr./hr.)	Specific yield (μM./l./kr.)
24	2.74	350
5	2.74	184

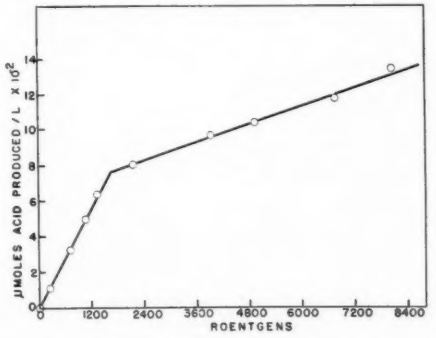

FIG. 1. Irradiation of 1 molar chloral hydrate solution with Co^{60} gamma-rays (dose rate = 1.08 kr./hr.).

centigrade, and the temperature varied by one or two degrees from experiment to experiment, the results have been corrected to 25°C. unless otherwise stated. The results of a typical irradiation experiment, using a constant dose rate of 1.08 kr./hr. are shown in Fig. 1.

It was found that the amount of acid initially varied linearly with the total dose received by the solution (at constant dose rate). However, with a dose rate of 1.08 kr./hr., after about 1600 roentgens had been received by the solution, the specific yield (μM./l./kr.) decreased to one-fifth of its original value and then stayed constant up to 8000 roentgens.* This decrease in specific yield was shown to be related to depletion of the oxygen content of the solution (see Table II and Fig. 2). When a solution that had been irradiated until the specific yield had fallen off had oxygen bubbled through it, the specific yield increased to the value shown by a fresh solution through which oxygen was bubbled before irradiation. Bubbling oxygen through a fresh solution before

TABLE II
EFFECT ON ACID PRODUCTION OF BUBBLING OXYGEN THROUGH THE SOLUTION

Treatment with respect to oxygen	Total dose received, r.	Acid produced, μmoles acid/l.
No oxygen bubbled in	900	438
No oxygen bubbled in	1820	837
No oxygen bubbled in	2860	878
Oxygen bubbled in initially and then irradiated	918	323
Oxygen bubbled in after receiving 900 r.	1860	775
Oxygen bubbled in after receiving 900 r.	2830	1139
Oxygen bubbled in after receiving 2860 r.	3770	1219

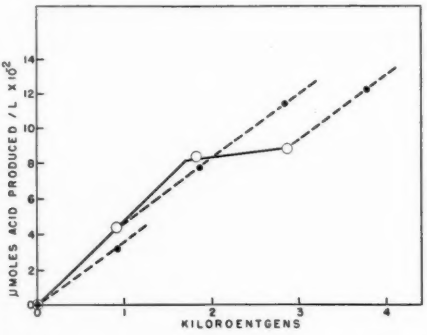

FIG. 2. Effect of oxygen on production of acid when 1 molar chloral hydrate is irradiated with Co^{60} gamma-rays.
——○—— No oxygen bubbled through the solution.
——●—— Oxygen bubbled through the solution.

**The initial specific acid yield with a dose rate of 1.08 kr./hr. was 467 μM./l./kr., but after about 1600 r., the specific acid yield decreased to 87 μM./l./kr.*

irradiation decreased the yield to about 75% of the value for air saturated solutions. The reason for this decrease is not known.

Solutions which were about four days old showed an induction dose of approximately 170 roentgens and then gave specific yields about 10% greater than those for fresh solutions. No induction period was observed with fresh solutions.

It was found that the acid concentration in the irradiated chloral hydrate solution did not change appreciably for at least $17\frac{1}{2}$ hr. after irradiation, if kept in the dark at room temperature. However, if kept exposed to light, the acid concentration slowly increased.

The effect of dose rate was investigated in a series of experiments. The results are recorded in Fig. 3. It was found that plotting the specific acid yield in

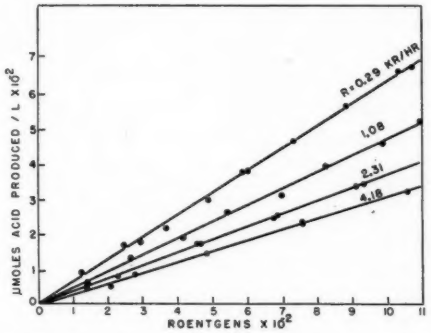

FIG. 3. Variation of yield of acid with dose rate using Co^{60} gamma-rays.

μM./l./kr. (Y) for a given dose rate, against the inverse of the square root of the dose rate in kr./hr., ($1/\sqrt{R}$) gave a linear relationship, $Y = 138 + 346/\sqrt{R}$, down to a dose rate of one kr./hr. (See Fig. 4.)

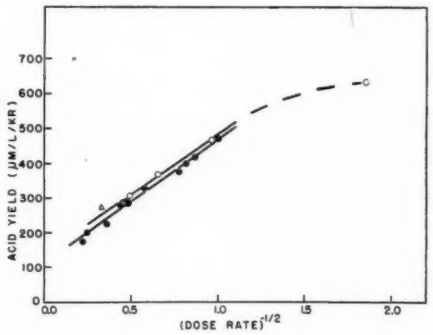

FIG. 4. Plot of yield of acid vs. (dose rate)$^{-\frac{1}{2}}$ for Co^{60} gamma-rays (○) and betatron X rays (●). △, Andrews and Shore.

Irradiation with Betatron X rays 23 Mev. Peak Energy (Results Corrected to 25°C.)

In experiments at a given dose rate, the acid production was proportional to the dose, as for Co^{60} γ-rays. The results are recorded in Fig. 5, as the best fitting straight lines. Only 7 of the 11 dose rates tried are shown, to avoid

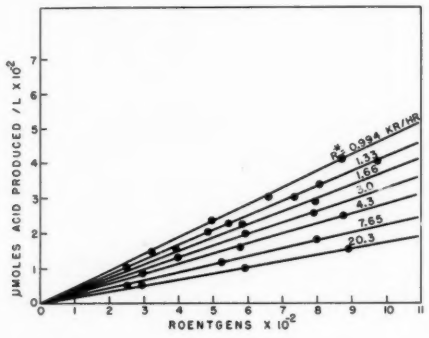

FIG. 5. Variation of yield of acid with dose rate and energy using betatron X rays, 25°C.

congestion in the figure. The precision was about the same for the betatron irradiations as for the Co^{60} irradiations. A plot of the specific yield, Y versus the inverse of the square root of the average dose rate $1/\sqrt{R^*}$ gave a reasonably straight line, the slope being practically the same as for Co^{60} (See Fig. 4). The equation of the line is $Y = 110 + (358/\sqrt{R^*})$. Changing the energy of the incident bremsstrahlung from 15 to 23 Mev. did not produce a significant change of specific yield of acid at a given dose rate (3).

The fact that the specific yield depends on the dose rate necessitated a further examination of the possible effects of rotating the samples in the betatron beam.

The X-ray beam was quite small in cross section and at a half angle (subtended at the target) of 3 degrees, the intensity was about 60% of that in the center of the beam. At the highest dose rates (16.6 and 20.3 kr./hr.) the lucite block was so close to the target that it was as wide as the 3 degree cone of the beam. As a result, the dose rate at a given position in the block varied by 40% as the block rotated. The dose rates received by various parts of the block when it was stationary were determined and plotted on polar coordinate paper. The curve through these points could be approximated by an ellipse, $R^2 = a^2b^2/(a^2 \sin^2\theta + b^2 \cos^2\theta)$, where R = dose rate, a = semimajor axis of ellipse, b = semiminor axis of ellipse, θ = angle between the line joining the center of the lucite block to the position of the sample and the direction of the beam through the center of the block. The angle θ varies between 0 and 2π.

Using this equation and the inverse square root relation as a first approximation, the yield for a given average dose rate, R^*, can then be determined.

Thus, when the elliptical variation in dose rate is taken into consideration, one obtains

$$Y = 110 + 358\,[a^2b^2/(a^2\sin^2\theta + b^2\cos^2\theta)]^{-1/4}.$$

When the block rotates, θ varies between 0 and 2π. Hence, it is necessary to solve the following integral:

$$Y = \left[\int_0^{2\pi}\left\{110 + 358\left(\frac{a^2b^2}{a^2\sin^2\theta + b^2\cos^2\theta}\right)^{-1/4}\right\}d\theta\right] \Big/ \int_0^{2\pi} d\theta.$$

The solution was obtained graphically. The maximum effect due to rotating the block is about 3% and is obtained when the block is closest to the target. That is, at the highest dose rate, when the block was closest to the target, the measured specific yield was about 3% higher than would be expected for a homogeneous beam of intensity equal to the average intensity of the experimental beam across the block. As the block is moved further away from the target (i.e. at progressively lower dose rates) the variation of dose rate across the block becomes progressively less because the beam becomes wider; hence $a \rightarrow b$, and the effect due to the rotating becomes negligible. Therefore, this factor would not decrease the slope of the line in Fig. 4 more than about 1 or 2%.

DISCUSSION

It is seen from Fig. 4 that the specific acid yield varies inversely as the square root of the dose rate down to a dose rate of about one kr./hr. Andrews and Shore (1) reported dose rate independence. However, the fact that they observed no dose rate dependence may be due to the high dose rates used and the great thickness of sample used in the experiments. The Andrews and Shore point plotted in Fig. 4 was obtained by multiplying the slope of the 1 *M* line in Fig. 1 of their paper by 1.30, which is the average ratio for (total acid from titration)/(HCl from conductance) obtained from Table I of their paper (1). Although this point was determined using 200 kv. X rays most of the difference between their result and those reported here is probably due to the dose rate effect.

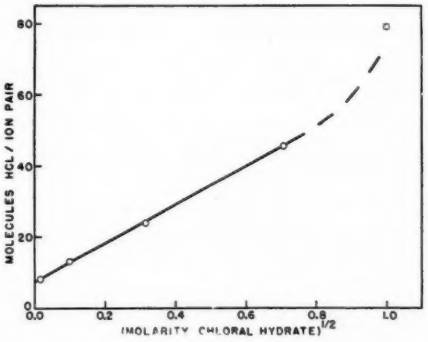

FIG. 6. Variation of specific yield of acid with chloral hydrate concentration (using the results obtained by Andrews and Shore).

Andrews and Shore (1) investigated the dependence of the specific yield of acid upon the concentration of chloral hydrate. In Fig. 6, their results have been plotted against the square root of the chloral hydrate concentration. (The values for M/N and the chloral hydrate concentration were obtained from Figs. 1 and 2 of their paper (1).) The variation is linear, except for the most concentrated solution. The equation of the line in Fig. 6 is: $M/N = 54.3\sqrt{c} + 7.3$, where c = chloral hydrate concentration (molarity).

The ion pair yield for the reaction with 1 M chloral hydrate is about one hundred and a free radical-chain reaction must be postulated to explain this high yield. The decrease in the yield with increasing dose rate is probably due to an increasing amount of reaction of free radicals with themselves. The fact that the yield is inversely proportional to the square root of the radiation intensity over quite a wide range of dose rates indicates that a recombination process, second order with respect to the atoms or radicals concerned, is probably playing an important part in the mechanism and in fact must be the principal process by which those atoms or radicals disappear (8). A comparison of our results with Noyes and Leighton's limiting cases 3 and 4 (8, pp. 196 and 197), seems to indicate that the recombinations of both primarily and secondarily produced radicals are of comparable importance in breaking chains.

It is also seen from Fig. 4 that for the same dose rate the yield of acid in one molar chloral hydrate solution is very nearly the same whether Co^{60} γ-rays (average energy 1.25 Mev.) or betatron X rays (peak energies from 15–23 Mev.) are used.

The Co^{60} line lies above the betatron line. This difference may be due to an energy dependence of the system. On the other hand it may be due to factors such as uncertainties in Victoreen dose determinations at high energies, or the pulsed nature of the betatron X rays (emitted in pulses at the rate of 180 per second, each pulse lasting 4 μseconds). Each factor will be discussed in turn.

The possibility that the system is energy dependent does not appear to be very likely since no significant difference was noted between the yields obtained for 15, 22, and 23 Mev. peak energies with the betatron for the same dose rate. The median energies of the 15, 22, and 23 Mev. peak X rays are approximately 5, 8, and 8.8 Mev., respectively. That no significant difference was observed is reasonable since the energies for both Co^{60} γ-rays and the betatron X rays are mainly in the region where energy is absorbed principally by the Compton process. Using the Compton and pair production coefficients for water and the photon energy distribution given by Cormack and Johns (2) it was calculated that about 11% of the beta particles (counting both positrons and negatrons) were produced by the pair process using 25 Mev. peak energy X rays from the betatron. The percentage of pair particles decreases with decreasing photon energy. Hence, in this energy region the chemical effect should not depend significantly on the energy of the incident radiation but only on the amount of energy absorbed by the system. A similar result has been found for several other reactions (4, 5).

The Victoreen condenser r.-meter is accurate to 2% over the energy range, 30 kev. to 1 Mev. (9). However, the accuracy of the calculation of energy absorption from Victoreen readings for energies above 1 Mev. is not known and this is therefore a possible source of error.

The betatron X rays are emitted in 4 μ second pulses at the rate of 180 per second. Therefore, for an average dose rate of 1 kr./hr., the actual dose rate in each pulse is 1400 kr./hr. One can readily see from Fig. 4 that for a steady dose rate of 1400 kr./hr. the yield of acid would be considerably less than that actually observed for an intermittent dose rate of 1400 kr./hr. In actual fact, the yield of acid observed for the intermittent dose rate of 1400 kr./hr. was only slightly less than the yield observed for the steady dose rate of 1 kr./hr. with Co^{60} gamma-rays. Thus, if the variation of acid yield with dose rate is attributed to reaction of free radicals with themselves, then the concentration of free radicals present in the solution when it is irradiated with Co^{60} gamma-rays at the rate of 1 kr./hr. must be nearly the same as when it is irradiated with betatron X rays at the intermittent rate of 1400 kr./hr. (i.e. average rate of 1 kr./hr.). This must mean that the free radical-chains have a significant lifetime and that their concentration builds up as irradiation proceeds, and reaches a constant value after a certain time (8). If the average lifetime was appreciably less than 1/180 sec., their concentration would instantaneously become very large and then fall off to zero with each pulse. However, if the average lifetime of the free radicals was greater than 1/180 sec., their concentration could build up under irradiation until it reached a more or less steady state. This would tend to cancel the effect of the pulses. With Co^{60} gammas, the free radical concentration would build up to a similar value for the same average dose rate, and one would expect similar acid yields. Since the acid yields observed for the same average dose rates are nearly the same, it is reasonable to suggest that the free radical-chains produced in this system have an average life greater than 1/180 sec. The effect of the pulses could easily account for the difference in the betatron and Co^{60} lines in Fig. 4.

It is concluded from the foregoing considerations that in the reaction of X or gamma-rays with aqueous 1 *M* chloral hydrate solutions the specific yield is independent of the energy over the energy range used, but dependent on the intensity of the incident radiation in the range investigated. The specific yield is also dependent on the temperature of the solution. The reaction is a chain reaction.

ACKNOWLEDGMENTS

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SOME FATTY ACIDS OF PEANUT, HICKORY, AND ACORN OILS[1]

By C. Y. Hopkins and Mary J. Chisholm

ABSTRACT

Eicosenoic and docosenoic acids have been identified as constituents of the glycerides of peanut oil (*Arachis hypogaea* L. var. Spanish). Hexadecenoic acid could not be detected; if present, the amount in this sample of oil is judged to be less than 0.3% of the fatty acids. The oils of the bitter hickory nut (*Carya cordiformis* Koch) and acorn (*Quercus alba* L.) have the ordinary palmitate–oleate–linoleate composition. Neither contained a detectable amount of eicosenoic acid. Estimated proportions of some of the acids in these oils are given.

INTRODUCTION

The occurrence of *n*-eicosenoic acid in plant glycerides has been noted chiefly in members of the Cruciferae family. Indications of its presence in other plant groups have been obtained but positive identification has rarely been made (3, 4, 11).

The present work was undertaken to determine whether eicosenoic acid is present in three species of seeds, representing three different plant families, namely the peanut (Leguminosae), hickory (Juglandaceae), and acorn (Fagaceae). The peanut was chosen as a probable producer of eicosenoic acid, $C_{20}H_{38}O_2$, because it is known to contain arachidic acid $C_{20}H_{40}O_2$.

An earlier report of eicosenoic acid in the filbert (4), although not confirmed (2), gave some grounds for believing that other nut trees might produce this acid. Two species of native trees were therefore included in the study.

The oils were extracted in the laboratory, converted to methyl esters and distilled fractionally *in vacuo*. The appropriate fractions were examined for eicosenoic acid and some attention was given to the other component acids.

EXPERIMENTAL

A. Peanut Oil

Raw shelled peanuts were purchased locally (*Arachis hypogaea* L. var. Spanish). On solvent extraction, they yielded 42% of oil having iodine value 100.7, saponification value 190, and unsaponifiable matter 0.7%. The oil was converted to methyl esters by methanolysis, using a variation of the method of Haller (5), as follows:

Absolute methanol (1000 gm.) was weighed with its container and dry HCl was bubbled in until 20 gm. of HCl had been absorbed. The oil (500 gm.) was added and the mixture was refluxed for 24 hr., then cooled in a separatory funnel. The upper layer (A) was removed and distilled on a steam bath until the volume was reduced to half. The concentrate was poured into four volumes of water and to this solution was added the lower layer (B). The esters were extracted from this mixture by ether.

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Examination of Low Boiling Esters

A quantity of the methyl esters (241 gm.) was distilled at reduced pressure through a column packed with metal rings. The first fraction, b.p. 102–107° at 0.1 mm., weight 14.4 gm., I.V. 10.4, was examined for hexadecenoate. It was crystallized from acetone, yielding mostly esters of saturated acids. The portion soluble at −60° (3.3 gm.) had I.V. 100.5. It was hydroxylated by permanganate but gave only dihydroxy- and tetrahydroxy-stearic acids, identified by mixed melting point with authentic samples. Thus the chief unsaturated acids in this fraction are oleic and linoleic. The amount of hexadecenoic acid in this sample of oil, if present at all, is estimated to be less than 0.3% of the total fatty acids.

Identification of Eicosenoic Acid

A quantity of methyl esters of peanut oil (780 gm.) was distilled fractionally until most of the esters of C_{16} and C_{18} acids had distilled off. The residual esters (88 gm., I.V. 45.6) were transferred to a smaller flask and fractionated as shown in Table I. The time:temperature curve for the distillation is plotted in Fig. 1.

TABLE I
DISTILLATION OF HIGHER-BOILING METHYL ESTERS OF PEANUT OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	127–130	13.4	99.6
2	130–143	4.0	72.2
3	143–150	17.9	42.6
4	150–157	5.7	15.3
5	157–165	20.0	4.0
6	165–176	6.2	5.9
7	(*a*)	2.4	
R	Residue	16.8	68.5
		86.4	

(*a*) *Portion obtained by rinsing the column packing.*

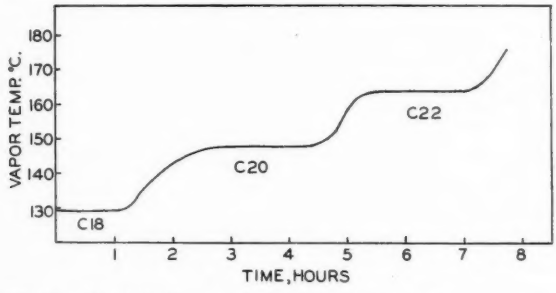

FIG. 1. Distillation of high-boiling methyl esters of peanut oil.

Fractions 1, 3, and 5 were judged from the boiling range and the time:temperature curve to contain esters of C_{18}, C_{20}, and C_{22} acids respectively. Fraction 3 was crystallized from acetone and gave the following fractions:

Fraction	Temp. of cryst'n., °C.	Yield, gm.
31	0	9.0 M.p. 44–46°C.
32	−32	1.6 I.V. 63.3
33	−50	2.7 I.V. 71.8
34	Filtrate	3.2 I.V. 103.3

Fraction 31 is evidently the ester of a saturated acid. The melting point corresponds to that of methyl arachidate.

Fraction 33 was saponified and hydroxylated by alkaline permanganate. After removal of saturated acids by hexane, the product was crystallized from ethyl acetate. It melted at 129–130°, alone and mixed with an authentic sample of 11,12-dihydroxyeicosanoic acid.* Its equivalent weight was 344.6 (theory 344.5). The principal unsaturated acid of fraction 33 is therefore eicosenoic acid.

Fraction 2 (Table I) was hydroxylated in the same way. The product had m.p. 118–120° and equiv. wt. 329, apparently a mixture of dihydroxystearic and dihydroxyeicosanoic acids.

It is estimated from these data that the original methyl esters contained about 12 gm. of methyl eicosenoate or about 1.6% of the total esters of peanut oil.

In order to obtain a further quantity of the eicosenoic acid, 1460 gm. of the methyl esters was distilled fractionally in the usual way. The C_{20} fraction was purified by crystallizing from acetone and the methyl eicosenoate was hydroxylated. The resulting dihydroxyeicosanoic acid was subjected to oxidative cleavage by sodium periodate (1). The products were nonaldehyde (the semicarbazone melted at 98–99°) and 10-aldehyodecanoic acid (the semicarbazone melted at 160–161°). The identities of both were confirmed by mixed melting points. Accordingly, the original acid is 11-eicosenoic acid.

Arachidic Acid

Further examination of the data indicates that the ester of the C_{20} saturated acid, methyl arachidate, is concentrated in fractions 3 and 4 (Table I) and that the amount is about 1.5% of the total esters.

Identification of Docosenoic Acid

A portion of fraction 5 (14.5 gm.) (Table I) was crystallized from 360 ml. of acetone, giving the following fractions:

Fraction	Temp. of cryst'n., °C.	Yield, gm.
51	24	9.4
52	18	
53	6	2.2
54	−5	0.6
55	Filtrate	0.8, I.V. 59

**Melting points are not corrected.*

Upon hydroxylation with permanganate, fraction 55 gave an acid of m.p. 128–129°. The melting point was not depressed by mixing with pure 13,14-dihydroxybehenic acid but was lowered about 5° by mixing with dihydroxystearic or dihydroxyeicosanoic acid. Accordingly, the presence of docosenoic (erucic) acid in the original oil is established. The amount is estimated at 0.2% of the total fatty acids.

B. Hickory Nut Oil

Hickory nuts (*Carya cordiformis* Koch) were collected in Glengarry County, Ontario, in 1951. They were dried and shelled. The kernels, which are quite bitter, yielded 45% of oil by solvent extraction. The oil had I.V. 94.2, saponification value 191, and unsaponifiable matter 0.6%. It was converted to methyl esters and 300 gm. of the esters was distilled at a pressure of about 0.1 mm. Distillation data are given in Table II.

TABLE II
DISTILLATION OF METHYL ESTERS OF HICKORY NUT OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value	$n_D^{25°}$
1	87–105	3.0	20.6	1.4405
2	105–112	10.8	23.2	Solid
3	112–114	19.2	66.3	1.4473
4	114–116	47.4	95.4	1.4514
5	116	45.6	102.6	1.4522
6	116	16.3	103.6	1.4522
7	116	40.0	102.2	1.4521
8	116–117	33.3	101.5	1.4521
9	117–119	36.4	100.1	1.4520
10	119–121	18.6	97.6	1.4518
11	121–125	11.2	95.7	1.4518
12	(*a*)	3.5	88.1	1.4514
R	Residue	13.5		
		298.8		

(*a*) *Portion obtained by rinsing the column packing.*

The course of the distillation showed that the fatty acids were predominantly 18 carbons in chain length. Fractions 1 to 3, with low iodine value and low refractive index, indicate an appreciable content of palmitic and stearic acids. Fractions 4–12 have the characteristics of a typical oleate–linoleate mixture with the iodine number decreasing gradually because of the slightly lower boiling point of the linoleate. The refractive index continues to fall even in fraction 12, showing that there is little, if any, acid higher than C_{18} in this fraction.

A portion of fraction 7 was crystallized from acetone. It yielded 0.2 gm. methyl stearate, m.p. 38–39°, 6.9 gm. methyl oleate, I.V. 85.4 and 3.0 gm. of oleate–linoleate mixture, I.V. 138.4.

Fractions 3, 11, and 12 were saponified. The equivalent weight of the acids was 276, 283, and 282 respectively (oleic acid 282.5). It is unlikely, therefore, that any acids higher than C_{18} are present in fractions 1–12.

The residue from the distillation was saponified and unsaponifiable matter was removed. The acids were crystallized from acetone giving the following fractions:

Fraction	Temp. of cryst'n., °C.	Yield, gm.	M.p., °C.	Equiv. wt.
R1	+15	0.3	64–66	319
R2	−35	1.1	59–61	301
R3	−52	4.3	Liq.	286
R4	Filtrate	4.9	Liq.	294

R1 and R2 are almost entirely saturated and consist of stearic and arachidic or behenic acids, judging by the equivalent weight.

R3 and R4 had I.V. 85.3 and 102.2 respectively. Efforts to crystallize R3 and R4 were not successful, the products being gummy. It is judged from the iodine values and equivalent weights that the content of monoenoic acids higher than C_{18}, if any are present, must be less than 1.0% of the total acids.

C. Acorn Oil

Acorns were gathered in the vicinity of Ottawa in 1951 from the white oak (*Quercus alba* L.). They were shelled and dried. The kernels yielded 4.6% of reddish-brown oil by solvent extraction. It had I.V. 109.7, saponification value 185, and unsaponifiable matter 3.7%.

The oil was converted to methyl esters (129 gm., I.V. 108.3). The esters were distilled at a pressure of about 0.1 mm. until 15 gm. remained in the pot. At this point 30 gm. of pure methyl erucate was added and the distillation was continued (Table III), in order to distill over esters of C_{18} and C_{20} acids if present.

TABLE III
DISTILLATION OF METHYL ESTERS OF ACORN OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value	$n_D^{25°}$
1	90–108	3.1	25.8	1.4430
2	108–112	10.4	33.3	solid
3	112–115	14.0	92.1	1.4508
4	115	12.5	119.1	1.4540
5	115	14.3	125.1	1.4550
6	115	16.0	125.9	1.4550
7	115–118	14.0	125.9	1.4550
8	118–120	16.0	124.4	1.4550
9	120–125	4.3	122.5	1.4549
10	125–128	9.0	119.7	1.4545
	Added 30 gm. methyl erucate			
11	110–128	6.8	101.6	1.4549
12	128–137	2.9	70.8	1.4550
13	137–146	3.0	70.8	1.4548
14	146–151	5.7	70.9	1.4548

The distillation follows the pattern of a typical palmitate–oleate–linoleate oil, although with more linoleate than in the hickory nut oil. There was no indication of a C_{20} fraction.

Fraction 1 was crystallized from acetone and then saponified, giving 1.1 gm. of solid acids, equiv. wt. 260. The mixed acids from fraction 2 had equiv. wt. 264.

Fraction 10 (methyl esters) was crystallized from acetone, giving the following portions:

Fraction	Temp. of cryst'n., °C.	Yield, gm.	Properties of esters
10–1	−27	0.2	M.p. 37–38
10–2	−50	2.8	I.V. 83.6
10–3	Filtrate	5.0	I.V. 146.1

Fraction 10–1 corresponds in melting point to methyl stearate. Upon hydroxylation with permanganate, fraction 10–2 readily gave dihydroxystearic acid, m.p. 129.5–130.5° alone and mixed with 9,10-dihydroxystearic acid. Therefore, the chief monoenoic acid in this fraction was ordinary oleic acid. The iodine value of fraction 10–3 shows that it is mainly polyenoic acid, probably linoleic.

A portion of fraction 11 was crystallized from acetone at −50°C. The crystals, 2.3 gm.; I.V. 73.9, were saponified and hydroxylated by permanganate. The product, after several crystallizations, melted at 127–129°. When mixed with 9,10-dihydroxystearic acid, it melted at 127–129°; with 11,12-dihydroxyeicosanoic acid it melted at 120–124°. It is concluded that the chief monoenoic acid in fraction 11 is ordinary oleic acid. The esters from the acetone filtrate (3.4 gm.; I.V. 115.9) were also saponified and hydroxylated. The portion of the product insoluble in ethyl acetate was tetrahydroxystearic acid, m.p. 171–173° alone and mixed with an authentic sample. Thus fraction 11 is shown to contain mainly oleic and linoleic acids.

Fraction 12, on hydroxylation, gave dihydroxybehenic acid, presumably arising from the methyl erucate that was added during the distillation. There was no evidence of eicosenoic acid.

DISCUSSION

A. Peanut oil fatty acids have been studied at various times with some variation in results attributable to varietal or regional differences. Recent workers agree fairly well on the proportions of fatty acids present except for hexadecenoic acid. The present work, however, is the first in which eicosenoic and docosenoic acids are identified.

The presence of eicosenoic acid was suspected because of the known content of C_{20}–C_{24} saturated acids. Eicosenoic and docosenoic acids tend to occur together. In this oil, the docosenoic acid is the lesser of the two in amount.

As in most vegetable oils, the acids of lower molecular weight (below C_{18}) are predominately saturated. We were unable to find hexadecenoic acid in

the present sample although it has been reported by others (6, 8). Wikoff and co-workers did not find hexadecenoic acid in their examination of peanut oil (12).

Arachidic acid is estimated in the present sample as 1.5% of the total fatty acids. This is a lower figure than is commonly quoted. Actually, peanut oil is a poor source of arachidic acid. The present data, as well as those of Wikoff (12) and others, show that the peanut contains more behenic than arachidic acid.

It is clear that peanut oil differs from many oleate-type oils in having an appreciable content of acids higher than C_{18}, both saturated and unsaturated. Some legume oils exhibit this characteristic in varying degrees but it is by no means universal throughout the legume family.

B. Hickory nut oil, from a bitter species given as *Carya cordifornia*, was studied by Riebsomer and co-workers (10). They reported the mean molecular weight of the unsaturated acids as 317 but found only C_{16} and C_{18} acids upon further analysis. Palmitic, stearic, and oleic acids were positively identified by them but the tetrabromide test for linoleic acid was negative.

The present sample of oil from the bitter species *Carya cordiformis* Koch, was found by us to contain predominately C_{18} acids. Oleic acid was isolated (as the ester) and iodine values above 100 for fractions 5 to 9 are judged to be sufficient evidence for the presence of linoleic acid. The saturated acids were palmitic, stearic, and a small amount of higher acid. Neither eicosenoic nor docosenoic acids could be detected although there was an indication of a little monoenoic acid, other than C_{18}, in the distillation residue.

C. Acorn oils from two species of oak have been examined by earlier workers. An Indian species (*Quercus incana* Roxb.) was found to have 17% palmitic, 0.9% other saturated acid, and 82% oleic acid (9). The swamp oak (*Q. palustris* Muench) gave an oil which had 15% saturated acids, 58% oleic acid, and 27% linoleic acid (7).

In the present work, the oil of a third species, *Q. alba* L., was found to have a simple palmitate–oleate–linoleate composition. Oleic and linoleic acids were identified by chemical derivatives. Eicosenoic acid could not be detected.

CONCLUSIONS

The analysis of the three oils, although not complete, permits estimates of the proportions of some of the fatty acids. The figures are given as percentages of the total fatty acids.

Peanut oil: archidic 1.5, behenic 3.4, eicosenoic 1.6, docosenoic 0.2; hexadecenoic could not be detected—if present, less than 0.3.

Hickory nut oil: palmitic 6, stearic 1, higher saturated acids 0.5, oleic 72, linoleic 19; higher monoenoic acids could not be identified—if present, less than 1.0.

Acorn oil: palmitic 10, stearic 2, oleic 48, linoleic and other polyenoic 40; eicosenoic could not be detected—if present, less than 0.5.

11-Eicosenoic acid is therefore a minor constituent of this sample of peanut oil, constituting about 1.6% of the total fatty acids. It could not be detected

in the hickory and acorn oils. If present at all, the amount is judged to be less than 1.0% in the hickory oil and less than 0.5% in the acorn oil.

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PYRIDINE DERIVATIVES

PART VI*. MALONATIONS OF SUBSTITUTED NITROPYRIDINES[1]

By W. Gruber

ABSTRACT

5-Hydroxy-2-alkylpyridines (VII) were prepared by a sequence of reactions starting with the malonation of 2-chloro-5-nitropyridine with diethyl alkylmalonates. Malonation failed with 4-methoxy-3-nitropyridine (VIII) and 2-chloro-3-nitropyridine (XII), yielding decomposition products only. Reactivity of the methoxyl groups in 4-methoxy-3-nitropyridine (VIII) and in 2-methoxy-3-nitropyridine (XV) was compared with respect to the rearrangement to N-methylpyridone, the reaction with aromatic amines, and hydrolysis with dilute acids. Methylation of 2-hydroxy-3-nitropyridine yields either 2-methoxy-3-nitropyridine (XV) or N-methyl-3-nitro-2-pyridone (XVI) as can be expected.

In Part I of this series (5) it was shown that malonation of 2-chloro-5-nitropyridine gives in good yields diethyl(5-nitropyridyl-2)-ethylmalonate (I, R = Et). This compound was the intermediate for a synthesis of *d*-pseudoconhydrine (II), thus proving the structure of (II). In Part IV (4) the isomeric 3-hydroxy-2-alkylpyridines (III) have been synthesized by rearrangement of 2-acylfuranes with ammonia. This paper reports further applications of the malonation reaction on 2,5-, 2,3-, and 3,4-substituted pyridine derivatives.

The reaction was studied first with 2-chloro-5-nitropyridine. The best yields of (I) were obtained by heating the components without a solvent. At 80–100°C. a violent reaction took place which was moderated by gentle cooling. After the first reaction subsided the dark brown mixture was heated for one hour at 150°C. to complete the reaction. The cooled mixture was poured into water and extracted with ether. The solvent was evaporated and the residue distilled *in vacuo* so as to remove the starting material and also to distill the end product, provided its boiling point was not too high. (5-Nitropyridyl-2)-alkylmalonesters are highly viscous, yellow oils which did not crystallize. During hydrolysis of these malonesters with sulphuric acid (50% v/v) or 20% hydrochloric acid, complete decarboxylation occurred. The intermediate, (5-nitropyridyl-2)-alkylacetic acid (IV) is still more unstable than pyridyl-2-acetic acid (6,12), the nitro group in the 5-position increasing the lability. The 2-alkyl-5-nitro-pyridines (V) do not give picrates, having not enough base-strength, but some of them have been characterized as chloroplatinates.

The nitro group was reduced either with stannous chloride or by catalytical hydrogenation. Both methods yielded the 5-amino-2-alkylpyridines almost quantitatively. Except 5-amino-2-benzylpyridine (VI, R = $CH_2C_6H_5$) all of them were oils and were therefore characterized as monopicrates (Table I). By diazotization and hydrolysis of the diazoniumsulphate, the amines were converted into the 5-hydroxy-2-alkylpyridines (VII, R_1 = alkyl, R_2 = H), which showed the normal properties of aromatic phenols: Color reaction with

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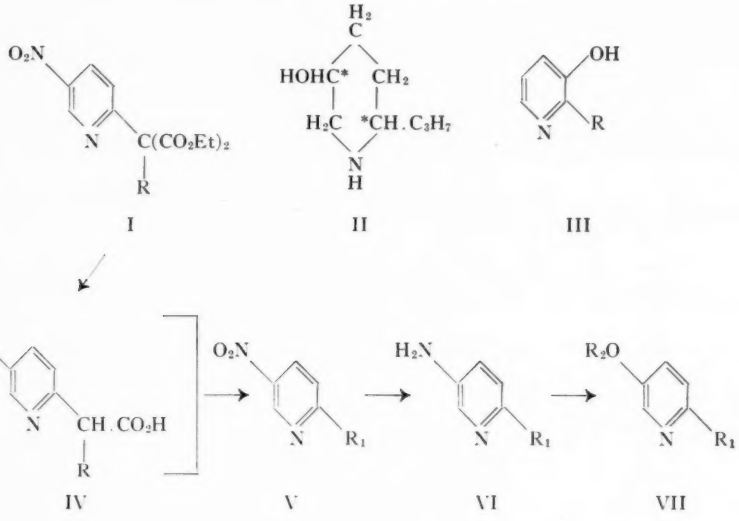


TABLE I

5-Amino-2-alkylpyridines VI	M.p., °C.	Analytical figures	
		Calc., %	Found, %
Picrate of 5-amino-2-ethylpyridine ($R_1 = C_2H_5$)	189–191	$C_7H_{10}N_2.C_6H_3N_3O_7$ N 19.94	20.12
Picrate of 5-amino-2-*n*-propylpyridine ($R_1 = n\text{-}C_3H_7$) (5)	163–165		
Picrate of 5-amino-2-*n*-butylpyridine ($R_1 = n\text{-}C_4H_9$)	142–143	$C_9H_{14}N_2.C_6H_3N_3O_7$ C 47.49 H 4.52	47.55 4.41
Picrate of 5-amino-2-*sec*-butylpyridine ($R_1 = sec\text{-}C_4H_9$)	151–153	$C_9H_{14}N_2.C_6H_3N_3O_7$ C 46.51 H 4.42 N 18.08	46.74 4.53 18.05
Picrate of 5-amino-2-*n*-amylpyridine ($R_1 = n\text{-}C_5H_{11}$)	150–152	$C_{10}H_{16}N_2.C_6H_3N_3O_7$ C 48.85 H 4.87 N 17.81	48.65 4.93 17.65
5-Amino-2-phenylethylpyridine ($R_1 = CH_2CH_2C_6H_5$)	113–115	$C_{13}H_{14}N_2$ C 78.75 H 7.12 N 14.13	78.55 7.13 14.27

ferric chloride solution produced red to brown complexes, and coupling with *o*- and *p*-nitroanilines gave brown azo dyes.

Compounds of type (VII) are readily soluble in 1 *N* alkali and 1–2 *N* acids (Table II).

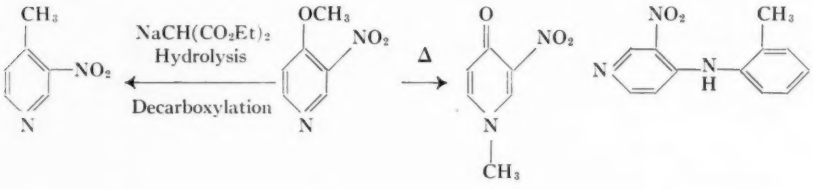
TABLE II

5-Hydroxy-2-alkylpyridines VII	M.p., °C.	Analytical figures	
		Calc., %	Found, %
5-Hydroxy-2-ethylpyridine (R_1 = C_2H_5, R_2 = H)	129–131	C_7H_9NO	
		C 68.27	68.26
		H 7.37	7.36
		N 11.37	11.35
5-Hydroxy-2-*n*-propylpyridine (R_1 = *n*-C_3H_7, R_2 = H) (5)	92–94		
5-Hydroxy-2-*n*-butylpyridine (R_1 = *n*-C_4H_9, R_2 = H)	83–85	$C_9H_{13}NO$	
		C 71.49	71.39
		H 8.67	8.60
		N 9.26	
5-Hydroxy-2-*sec*-butylpyridine (R_1 = *sec*-C_4H_9, R_2 = H)	96–98		71.27
			8.76
3,5-Dinitrobenzoate (R_1 = *sec*-C_4H_9, R_2 = 3,5-$(NO_2)_2C_6H_3CO$-)	133–135	$C_{16}H_{15}N_3O_6$	9.50
		C 55.65	55.44
		H 4.38	4.32
		N 12.17	12.15
5-Hydroxy-2-*n*-amylpyridine, 3,5-Dinitrobenzoate (R_1 = *n*-C_5H_{11}, R_2 = 3,5-$(NO_2)_2C_6H_3CO$-)	98–101	$C_{17}H_{17}N_3O_6$	
		C 56.82	56.75
		H 4.71	4.82
		N 11.70	11.52
5-Hydroxy-2-phenylethylpyridine (R_1 = $CH_2CH_2C_6H_5$, R_2 = H)	148–150	$C_{13}H_{13}NO$	
		C 78.36	78.20
		H 6.58	6.45
		N 7.03	7.14

4-Chloro-3-nitropyridine does not seem to be stable (9) (4-chloropyridine is also unstable according to Wibaut and Broekman (11)). The malonation of "4-chloro-3-nitropyridine hydrochloride with diethyl disodiomalonate" reported by Koenigs and Fulde (7) was almost certainly a malonation of 4-methoxy-3-nitropyridine hydrochloride, in view of a later paper by Bremer (3), who prepared 4-methoxy-3-nitropyridine (VIII) *in situ* by pouring a mixture of 4-hydroxy-3-nitropyridine and phosphorus pentachloride into cooled methanol. The methoxyl group was highly reactive, so that this stable compound could be used as starting material for many reactions instead of the unstable halide. Bremer did perform the malonation of (VIII) with diethyl sodiomalonate, which yielded 4-methyl-3-nitropyridine (IX).

The synthesis of (VIII) was repeated in the hope of establishing a general method for the synthesis of 3-nitro-4-alkylpyridines, but we could not achieve the desired malonation with substituted diethyl malonates. The identity of the starting material was checked by its rearrangement to N-methyl-3-nitro-4-pyridone (X) and by its reaction with *o*-toluidine to yield N-(3-nitropyridyl-4)-*o*-toluidine (XI) quantitatively. Malonation of (VIII) was attempted with diethyl sodiomethylmalonate and diethyl sodio-*i*-propylmalonate using ether,

ethanol, or benzene as a solvent. After reduction of the supposed nitro-compound, the amine, which was obtained as an oil, was characterized as a picrate which was the same in both cases, but identical neither with that of 3-amino-4-hydroxypyridine nor that of 3-aminopyridine. This picrate (Substance P) is now believed to derive from a base generated during the reaction by decomposition of the pyridine nucleus.

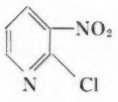


IX VIII X XI

Finally, malonations were tried with 2-chloro-3-nitropyridine (XII). Although the components reacted violently and the reaction mixture gave a positive test for chloride ion, the desired (3-nitropyridyl-2)-alkylmalonate could not be isolated, probably because (XII) decomposed. According to Baumgarten and Chien-Fan Su (1) the reaction of 2-chloro-5-nitropicolin (XIII) with sodium methylate gave 2-methoxy-5-nitropicolin in high yield, whereas the same reaction with the 2,3-isomer (XIV) brought about only decomposition. From these facts it was concluded that all chloro-nitropyridines with substituents in ortho position react in a similar way; however, the reaction of 2-chloro-3-nitropyridine (XII) with sodium methoxide yields the methoxyl compound (m.p. 57–58°C.) almost quantitatively. 2-Methoxy-3-nitropyridine (XV) has been reported in the literature (8) to have a m.p. of 110°C. It was prepared from the silver salt of 2-hydroxy-3-nitropyridine and methyl iodide and it is well known from methylation experiments on 2-hydroxy-5-nitropyridine (2) that this silver salt method gives rise not only to the methyl ethers but also to the N-methyl-nitropyridones. The methylation of 2-hydroxy-3-nitropyridine with methyl iodide via Ag-salt was therefore repeated and 2-methoxy-3-nitropyridine (XV) as well as N-methyl-3-nitro-2-pyridone (XVI) could be separated from the reaction mixture. The methyl ether (XV) from this experiment was identical with the compound prepared by methylation of the halide (XII) with sodium methoxide. The methylation of the potassium salt of 2-hydroxy-3-nitropyridine with methyl sulphate produced mainly the pyridone (XVI), which again was identical with the compound, prepared by methylation of the silver salt.

The reaction of (XII) with aliphatic and aromatic amines proceeds normally.

To compare the reactivity of the methoxyl groups in (VIII) and (XV) attempts were made to rearrange 2-methoxy-3-nitropyridine (XV) to N-methyl-3-nitro-2-pyridone by heating *in vacuo* in a sealed tube. Such a rearrangement would be expected by analogy with XVII → XVIII, (10), but the reaction failed. Unlike (VIII) the 2-methoxyl group in (XV) would react



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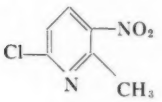

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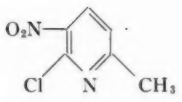

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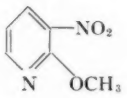

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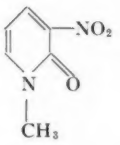
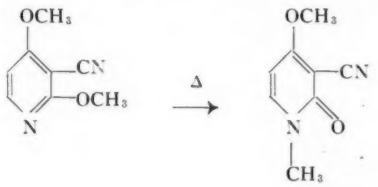


XVI

neither with *o*-toluidine nor piperidine at 130°C., but could be hydrolyzed easily even with 0.5 *N* acid at the steam bath for two hours.



XVII XVIII

EXPERIMENTAL*

The following are a few typical examples of the malonation reaction and of subsequent steps.

Diethyl (5-nitropyridyl-2)-methylmalonate (I, $R = CH_3$)

Diethyl sodiomethylmalonate was prepared by refluxing a mixture of 1.2 gm. of finely powdered sodium and 8.7 gm. of diethyl methylmalonate in 100 ml. of absolute ether. After complete dissolution of the sodium sand (10 hr.) the solvent was evaporated, the residue dried overnight in a desiccator, intimately mixed with 8 gm. of 2-chloro-5-nitropyridine, and cautiously heated on the steam bath. At 90°C. (thermometer in the mixture) a violent reaction set in and the content of the flask darkened. After the reaction subsided the mixture was heated to 150°C. (oil bath) for one hour, cooled, and 200 ml. of water added. The solution was extracted exhaustively with ether, the solvent evaporated and the residue distilled at 1 mm. The fraction above 150°C. (air bath temperature) was collected and redistilled; yield: 8.7 gm. (58%). Calc. for $C_{13}H_{16}N_2O_6$: N, 9.46%; Found: N, 9.70%.

5-Nitro-2-n-amylpyridine (V, $R_1 = n\text{-}C_5H_{11}$)

Diethyl (5-nitropyridyl-2)-*n*-butylmalonate (I, R = n-C_4H_9) (15.5 gm.) was heated to 110–120°C. with 90 ml. of sulphuric acid (1:1) until evolution of gas bubbles ceased (four hours). After cooling, the dark solution was ex-

**Melting points are corrected. Analyses are by A. Bernhardt, MPI, Mühlheim (Ruhr), Germany.*

tracted with ether and the organic layer discarded. The acid layer was diluted and made alkaline and after exhaustive extraction with ether, the ether was evaporated and the residue distilled *in vacuo* (120–130°C. air bath, 2 mm. Hg); Yield, 7.0 gm., i.e. 68%.

Of this base 380 mgm. was dissolved in 2 ml. of 20% hydrochloric acid and added to 3 ml. of a solution containing 350 mgm. H_2PtCl_6. The precipitate was thoroughly washed with very dilute hydrochloric acid and methanol. M.p. 152–155°C. (dec.); Yield, 578 mgm., i.e. 79%. Calc. for $(C_{10}H_{15}N_2O_2)_2$. $PtCl_6$: Pt, 23.89%. Found: Pt, 23.70%.

5-Nitro-2-n-butylpyridine (V, $R_1 = n\text{-}C_4H_9$)

This was synthesized as above. Chloroplatinate: m.p. 181–183°C. (dec.). Calc. for $(C_9H_{13}N_2O_2)_2$ $PtCl_6$: C, 28.06; H, 3.40; Pt, 25.34%. Found: C, 28.07; H, 3.27; Pt, 25.34%.

5-Amino-2-n-butylpyridine (VI, $R_1 = n\text{-}C_4H_9$)

A solution of 1.98 gm. of (V) ($R_1 = n\text{-}C_4H_9$) in 80 ml. of absolute methanol was shaken in a hydrogen atmosphere in the presence of 0.3 gm. of Adams' catalyst. The required amount of three moles of hydrogen (0°C., 760 mm. Hg, 739.2 ml.) was taken up in 15 min. The amine was isolated by filtering off the catalyst and evaporating the solvent and purified by distillation *in vacuo* (0.005 mm. Hg, 90–100°C. air bath). Yield: 1.64 gm. (almost quantitative). The picrate was prepared in ethereal solution from 300 mgm. of the base and 530 mgm. picric acid. Purification by several recrystallizations from methanol; m.p. 142–143°C.

5-Amino-2-phenylethylpyridine (VI, $R_1 = CH_2CH_2C_6H_5$)

A solution of 4.4 gm. of the nitro compound (V) ($R_1 = CH_2CH_2C_6H_5$) in 15 ml. of concentrated hydrochloric acid was added slowly to a cooled solution of 20 gm. of crystalline stannous chloride in 16 ml. of concentrated hydrochloric acid. After standing for one hour a strong sodium hydroxide solution was added in excess and then exhaustively extracted with ether. Purification by recrystallization from ether yielded 3.6 gm., i.e. 95%; m.p. 113–115°C.

5-Hydroxy-2-sec-butylpyridine (VII, $R_1 = sec\text{-}C_4H_9$, $R_2 = H$)

A solution of 1.26 gm. of (VII) ($R_1 = sec\text{-}C_4H_9$) in 90 ml. of 1 *N* sulphuric acid was diazotized with 0.8 gm. of sodium nitrite in 12 ml. of water, the yellow mixture was then heated on the steam for one hour and cooled. After the addition of solid sodium bicarbonate in excess, the solution was extracted with ether, the solvent evaporated, and the residue distilled *in vacuo*, giving a crude yield of 1.10 gm., i.e. 86%. This oil crystallized and was purified by several recrystallizations from ether – petroleum ether; m.p. 96–98°C.

The 3,5-dinitrobenzoate of this phenolic base was prepared by heating a mixture of 0.8 gm. of (VII) ($R_1 = sec\text{-}C_4H_9$, $R_2 = H$) and 1.3 gm. of 3,5-dinitrobenzoyl chloride for one hour on the steam bath. The cooled reaction mixture was taken up in ether, washed with 1 *N* sodium hydroxide and with water, then the solvent was evaporated. The residue was recrystallized twice from ether; m.p. 133–135°C.

N-(3-Nitropyridyl-4)-o-toluidine (XI)

4-Methoxy-3-nitropyridine (1.54 gm.) was heated with 1.07 gm. of *o*-toluidine on the steam bath until the mixture solidified completely (two hours). After cooling the mass was triturated with ether, filtered, and the residue recrystallized from dilute methanol; m.p. 85–87°C. Calc. for $C_{12}H_{13}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.76; H, 4.84; N, 18.12%.

2-Methoxy-3-nitropyridine (XV)

A solution of 1.4 gm. of 2-chloro-3-nitropyridine (XII) in 10 ml. of absolute methanol was shaken with sodium methoxide (from 0.3 gm. sodium and 5 ml. of methanol) for eight hours at room temperature, then refluxed for one hour, the solvent evaporated *in vacuo* and after addition of 100 ml. of water, the precipitate filtered with suction. After purification by vacuum distillation and recrystallization from ether – petroleum ether the m.p. was 57–59°C. Yield, 0.9 gm., i.e. 65%. Calc. for $C_6H_6N_2O_3$: C, 46.75; H, 3.93; N, 18.18; OCH_3, 20.13%. Found: C, 46.81; H, 4.05; N, 18.10; OCH_3, 20.05%.

Methylation of 2-Hydroxy-3-nitropyridine (XX)

(*a*) A solution of 0.60 gm. of (XX) in aqueous potassium hydroxide (0.25 gm. potassium hydroxide in 34 ml. of water) was mixed with aqueous silver nitrate solution (0.73 gm. silver nitrate in 2 ml. of water). The silver salt was isolated and dried; 800 mgm. was suspended in 8 ml. of methanol, 0.3 ml. of methyl iodide added, and the mixture refluxed overnight. The solvent was evaporated and the residue extracted twice with 10 ml. of cooled ether. After evaporation of the solvent and vacuum distillation of the residue, the m.p. was 57–58°C., not depressed by admixture of the methyl ether XV. Yield, 88 mgm., i.e. 18%, based on silver salt. The residue from the ether extraction weighed 286 mgm., i.e. 59%, and had a m.p. of 168–171°C. It was recrystallized several times from methanol–ether; m.p. 171–174°C.

(*b*) A mixture of 737 mgm. of (XX), 645 mgm. of potassium hydroxide, 633 mgm. of freshly distilled dimethyl sulphate, and 6 ml. of water was refluxed for six hours, cooled, the precipitate collected on a Büchner funnel and recrystallized twice from water. Yield, of N-methyl-3-nitro-2-pyridone, almost quantitative; m.p. 171–174°C. The mixed m.p. with the same fraction from (*a*) was not depressed. Calc. for $C_6H_6N_2O_3$: C, 46.75; H, 3.93; N, 18.18%. Found: C, 46.29; H, 3.82; N, 18.02%.

Acid Hydrolysis of XV

2-Methoxy-3-nitropyridine (257 mgm.) was heated with 20 ml. of 0.5 *N* hydrochloric acid on the steam bath for three hours. The oil disappeared slowly; cooling precipitated yellow crystals, m.p. 224–226°C.; no depression when mixed with 2-hydroxy-3-nitropyridine.

N-(3-Nitropyridyl-2)-o-toluidine

2-Chloro-3-nitropyridine (XII, 0.9 gm.) and *o*-toluidine (1.0 gm.) were heated at 150°C. for one hour. After removal of the excess of *o*-toluidine as hydrochloride, the residue was recrystallized from dilute methanol; m.p.

124–126°C. Calc. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84%. Found: C, 62.72; H, 5.00%.

ACKNOWLEDGMENT

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THE STABILITY OF RESIN EMULSIONS[1]

By L. A. Munro and F. H. Sexsmith

ABSTRACT

Accelerated settling tests were made on dilute polyvinyl acetate emulsions in the presence of increasing concentrations of electrolyte. Stability–electrolyte concentration curves for five of the six emulsions studied show a marked similarity to the zeta potential or mobility curves, indicating that under such conditions the charge on the latex particle is the most important factor in determining stability. The anomalous behavior of an almost neutral latex formulated with mixed cationic and nonionic emulsifiers is attributed to the preponderance of other factors associated with micellar phenomena.

In a previous paper (9) the authors have reported the effect of electrolyte concentration on the mobilities of polyvinyl latices prepared with cationic, anionic, and mixed emulsifying agents. With most of the emulsions, marked irregularities were found in the mobility–salt concentration curves. These irregularities were attributed to micellar phenomena. The zeta potentials calculated by the Henry modification of the Smoluchowski equation from the mobilities of a very uniform latex showed the same sharp minimum.

Reference to recent literature indicates that the dependence of the stability of colloidal suspensions or emulsions on particle charge or zeta potential is still being debated. Clayton (1) states that the stability of oil-in-water emulsions is a function of interfacial tension, Brownian movement, and particle charge. Ray and Hutchinson (10) consider that the zeta potential is the principal factor in the suspension stability of carbon particles in a dilute soap solution. Greiner and Vold (3) in their study of the suspending power of various surfactants for fine manganese dioxide powder, attribute stability to the zeta potential rather than to solubilization or to colloidality of the solution, except to the extent that micelle formation affects the concentration of simple ions.

Eilers and Korff (2) have attempted mathematically to relate electrical charge with stability of hydrophobic dispersions. They postulated a stability factor which varies with the square of the zeta potential and inversely as the Debye-Huckel function κ. The latter is an indication of the thickness of the ionic atmosphere. Concentrations of electrolyte too small to affect this factor may have an appreciable influence on the zeta potential.

Hayek (4) on the other hand reports no correlation between electrophoretic mobility and sol stability. He concludes from his work with dispersions in organic media that in such systems particle charges are incidental to but not responsible for the stability of the sols.

King has maintained that there is a lack of relationship between electrical charge and the stability of oil-in-water emulsions (5, 6). He suggested that there is an optimum degree of dispersion for maximum stability, which in turn is conditioned by the nature of the emulsifying or protective agent.

[1] *Manuscript received August 13, 1953.*
Contribution from Department of Chemistry, Queens University, Kingston, Ontario.

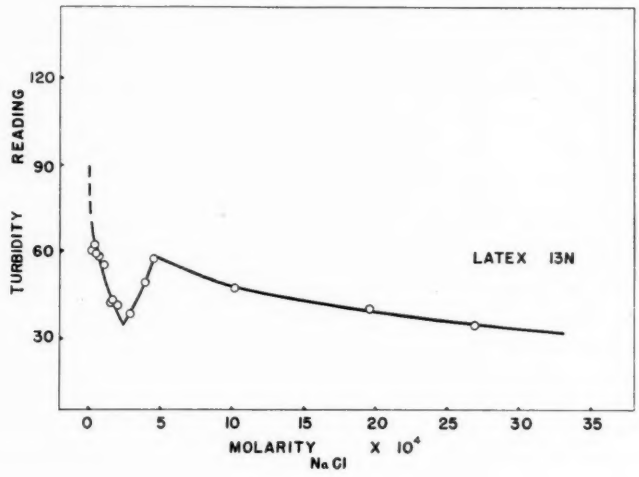

FIG. 1. Stability curve for latex 13N formulated with a nonionic emulsifier, hydroxyethyl cellulose.

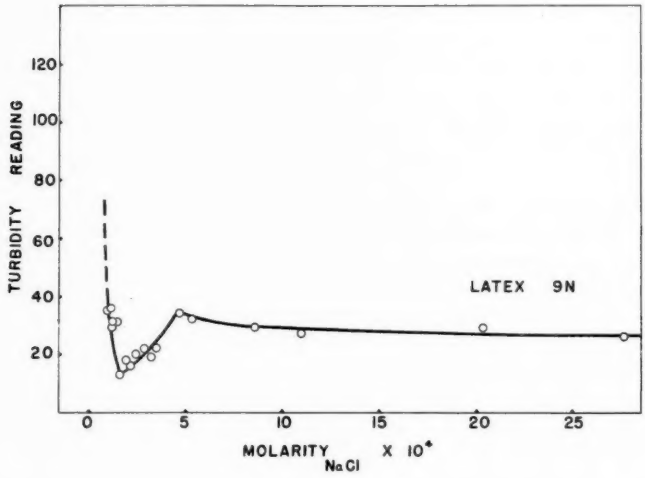

FIG. 2. Stability curve for latex 9N formulated with a nonionic emulsifier, polyvinyl alcohol.

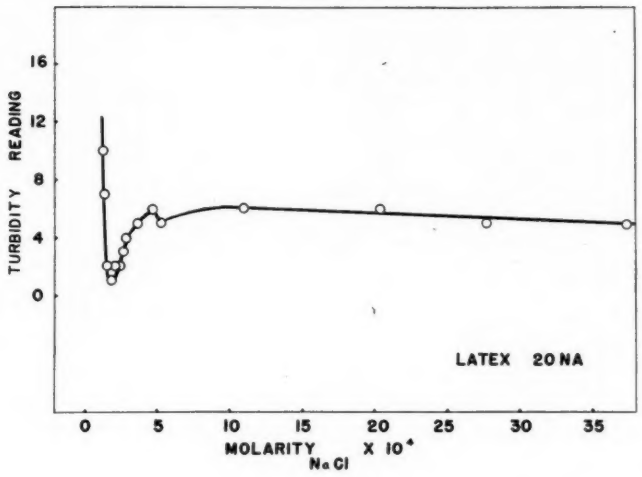

FIG. 3. Stability curve for latex 20NA formulated with mixed emulsifiers, gum tragacanth, and polyvinyl alcohol.

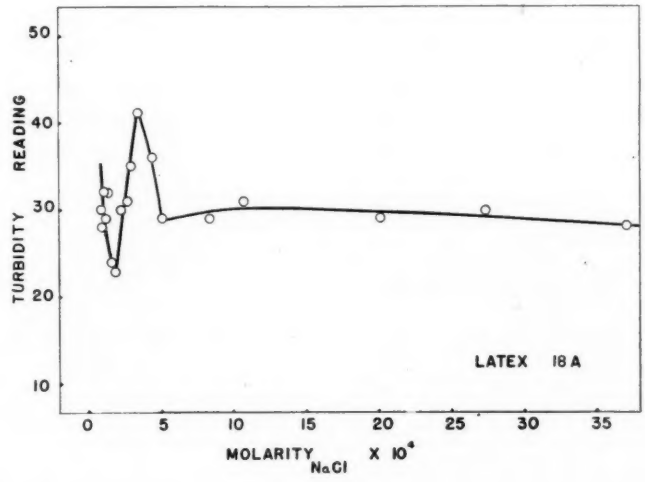

FIG. 4. Stability curve for latex 18A formulated with an anionic emulsifier, gum arabic.

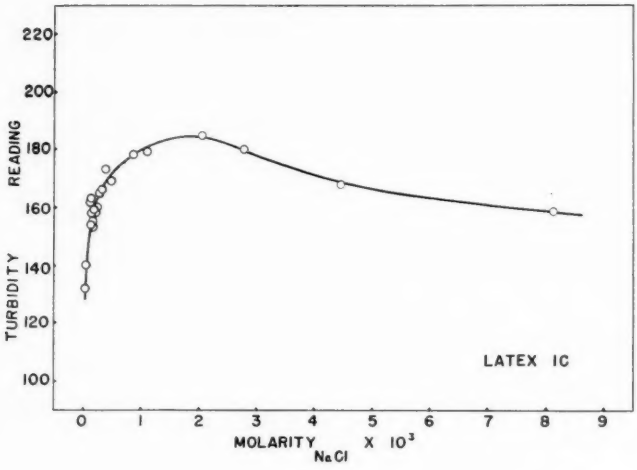

FIG. 5. Stability curve for latex 1C a commercial preparation (8).

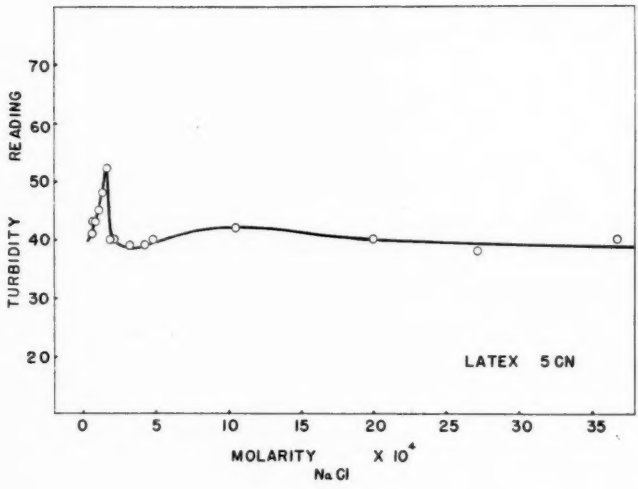

FIG. 6. Stability curve for latex 5CN a commercial preparation with mixed cationic and nonionic emulsifiers.

With the polyvinyl acetate latices used in our previous studies it was observed that there was a great divergence in primary stability. Some of the concentrated emulsions settled appreciably in a few hours while others showed very little settling after a week. Accelerated settling tests were set up with separate portions of the diluted emulsions used for the electrophoretic studies, or with samples of similar total resin content and identical electrolyte concentrations. It was felt that in addition to being of general interest, the peculiar shape of the mobility and zeta potential curves would facilitate the observation of any correlation between these quantities and the stability in such tests.

EXPERIMENTAL

Portions of the same samples used for electrophoresis or samples with similar resin content and the same electrolyte concentration were centrifuged for 30 min. in an Adams angle head centrifuge at 2070 r.p.m. The supernatant suspension was then decanted into fresh tubes and centrifuged for a further 10 min. Turbidity readings were made in a photoelectric colorimeter using a 342 blue filter. The scale reading was proportional to the total solids content for any given emulsion except for very dilute suspensions of polydisperse samples, where, as indicated by Morse (7) irregularities of particle size have a pronounced effect on turbidity. Initial concentrations of latex varied from 0.03 to 0.20%. Stability curves were obtained by plotting turbidity scale readings against salt concentration. These are shown in Figs. 1–6.

DISCUSSION

Reference to the previous paper (9) will show the remarkable similarity between the mobility curves and the curves for stability as indicated by the accelerated settling. In the case of latex 13N which was of very uniform particle size, the sharp minimum for turbidity occurs at 2.7×10^{-4} molar NaCl, for the zeta potential at 2.9×10^{-4}, and for the mobility at 2.5×10^{-4} M NaCl. While the other curves are subject to some error due to the variation in particle size, each of the emulsions 9N (Fig. 2), 20NA (Fig. 3), and 18A (Fig. 4) shows minimum turbidity at essentially the same concentration of electrolyte as that which gave minimum mobility. A comparison of the minima is given in Table I.

TABLE I

CONCENTRATION OF SODIUM CHLORIDE ($M \times 10^{-4}$) AT MINIMA FOR DIFFERENT EMULSIONS

Latex*	13N	9N	20NA	18A
Mobility	2.5	1.9	2.0	1.3
Stability	2.7	1.7	1.9	1.9

*13N *Nonionic emulsifying agent: hydroxyethyl cellulose.*
9N *Nonionic emulsifying agent: polyvinyl alcohol.*
20NA *Mixed nonionic and anionic: gum tragacanth and PVA.*
18A *Anionic emulsifying agent: gum arabic.*

The stability curve for latex 1C (Fig. 5) is also similar to its mobility curve. Each shows no minimum but a steep rise at low electrolyte concentration

reaching a broad maximum at salt concentration of approximately 20×10^{-4} molar (NaCl).

Latex 5CN (Fig. 6) formulated with mixed cationic and nonionic emulsifiers exhibited anomalous behavior in that the mobility and stability curves are entirely dissimilar. This emulsion had a very low standard mobility (8), and the stock emulsion (containing 55% solids) was the least stable of the 20 latices studied, giving a copious sediment in 24 hr. In contrast latex 1C showed no settling even after standing one week. The latter had the highest standard mobility of all the emulsions (8).

In the case of the initially unstable and almost neutral latex 5CN, the anomalous behavior is probably due to the preponderance of factors associated with micellar phenomena. One is inclined to agree with King's conclusion (6) that when no reaction takes place between electrolyte and emulsifying agent, the electrical charge on the dispersed globules does not determine stability. Under such conditions the initial settling depends more on size distribution, concentration of the latex, interfacial tensions, and the mechanical properties of the interfacial films than on particle charge.

While in the majority of cases the primary stability of concentrated emulsions of polyvinyl acetate can not be predicted from the mobilities at one standard salt concentration, the foregoing curves indicate that for dilute emulsions in the presence of electrolyte, the charge on the particle is the most important factor in determining stability.

ACKNOWLEDGMENT

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THE BIOGENESIS OF ALKALOIDS

IX. FURTHER INVESTIGATIONS ON THE FORMATION OF GRAMINE FROM TRYPTOPHAN[1]

By Edward Leete[2] and Léo Marion

ABSTRACT

A mixture of *dl*-tryptophan-2-C^{14} and *dl*-tryptophan-β-C^{14} with a known ratio of activity in the 2 and β positions was prepared. Feeding it to sprouting barley produced radioactive gramine which was isolated from the leaves. Systematic degradation of the alkaloid showed the activity to be present only in the 2 position of the nucleus and the methylene group of the side chain. The ratio of the activity in the two positions was the same as in the administered tryptophan. These results thus indicate that tryptophan is converted to gramine in the plant without cleavage of the indole–alanine linkage.

It was previously known that sprouting barley synthesized gramine, and it was shown (2) that feeding *dl*-tryptophan-β-C^{14} to the sprouting plant resulted in the formation of radioactive gramine in which the activity resided entirely in one position corresponding to that in which the C^{14} was located in the administered tryptophan. This result, strongly suggesting that tryptophan was the precursor of gramine, was somewhat surprising since gramine was formerly regarded as the only indole alkaloid that could not be derived from tryptophan by a simple biogenetic scheme, it being assumed that the alkaloid was produced in the plant by a method analogous to its *in vitro* synthesis from formaldehyde, indole, and dimethylamine (9). The experiment with *dl*-tryptophan-β-C^{14} did not exclude the possibility that the tryptophan might have been hydrolyzed to indole and serine, a reversal of its accepted biosynthesis (15, 16, 19). The serine could then have given rise to a one-carbon fragment which could conceivably have been utilized by the plant for a synthesis of gramine similar to the *in vitro* one.

This problem could be settled by feeding to the barley tryptophan labelled both in the indole nucleus and in the β-position of the side chain. Then, if any fission of the tryptophan occurred at the 3-position, one would not expect to obtain radioactive gramine in which the ratio between the activity in the indole nucleus and in the β-position was the same as in the administered tryptophan. The synthesis of *dl*-tryptophan-3-C^{14} has been described (7), the indole-3-C^{14} required for this synthesis being obtained in very poor yield from carbonyl-labelled benzoic acid. For the present work indole-2-C^{14} was prepared in two steps from radioactive sodium formate in 25% yield. The C^{14}-sodium formate was heated at 100° for 12 hr. with *o*-toluidine hydrochloride, *o*-toluidine, and inactive formic acid to give formyl-C^{14}-*o*-toluidine which was converted to indole-2-C^{14} by heating with potassium tertiary butoxide according to the method of Tyson (17, 18). A sample of the radioactive indole, diluted with

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[2] *National Research Council of Canada Postdoctoral Fellow.*

inactive indole, was converted to N-benzoylindole (20). This was oxidized with potassium permanganate to benzoylanthranilic acid (21) which was inactive, thus showing that all the activity in the indole resided in the 2-position. Tryptophan-2-C^{14} was prepared from this indole by established methods (1, 7, 13). Tryptophan-β-C^{14} was also prepared by the same methods using inactive indole and C^{14}-formaldehyde (2). A mixture of definite quantities of these two tryptophans constituted the doubly labelled tryptophan that was fed to the barley.

The initial feeding experiments were carried out by the previously described method (2), the tracer being added to the plant on the sixth day of sprouting and the leaves harvested on the 11th day. When the gramine was isolated it was found to be only weakly radioactive, the activity being too low to allow dilution with inactive gramine in order to make degradations possible. The only apparent differences between this experiment and that previously reported (2) were the state of development of the sprouting barley and the presence of much mold. Whereas in the former experiment the shoots were 5–6 cm. long on the sixth day of germination, they were 10–12 cm. long at the same time of growth in the present experiment, presumably owing to the higher temperature and humidity prevailing in the greenhouse. From these results it appears that the number of days after germination is probably not really significant, and that gramine is only synthesized in the plant during the initial growth of the leaves. It has been reported (3) that the quantity of gramine remains constant during the first 10 days, but that the alkaloid has disappeared after one month. That the more advanced development of the plant due to more rapid growth was indeed the reason for the lower activity in the isolated gramine was established by an experiment in which doubly labelled tryptophan was fed to the barley on the third day of germination, when the shoots were 1–1.5 cm. long, and the leaves were harvested on the ninth day of germination. From this experiment gramine of a high activity was obtained. The comparative results are summarized in Table I.

TABLE I
COMPARATIVE RESULTS

Experiment	Total activity of tryptophan fed to plant (disintegrations per min.)	Temperature of germination cabinet	Time of feeding tracer	Length of leaves at feeding time, cm.	Harvesting time	Activity of gramine (disintegrations per min. per millimole)
A	β-C^{14} 6.36×10^7	21–2° (March)	6th day of germination	5–6	11th day	1.02×10^5
B	2: β-C^{14} 5.67×10^7	27–32° (June)	6th day	10–12	11th day	7.9×10^3
C	2: β-C^{14} 3.59×10^7	27–32° (July)	3rd day	1–1.5	9th day	9.8×10^4

The gramine of high activity thus obtained was diluted with inactive gramine and degraded by essentially the same methods as those previously described (2) and by additional methods rendered necessary because of the labelling of the indole nucleus. The degradations carried out are illustrated in Fig. 1. The

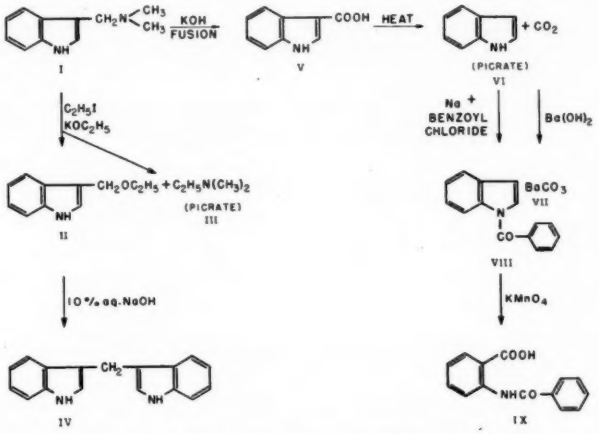


FIG. 1. Degradation of the gramine to determine the location of the radioactivity.

fusion of the gramine with potassium hydroxide gave rise to indolyl-3-carboxylic acid (V) which was decarboxylated to radioactive indole (VI) and radioactive carbon dioxide. The benzoyl derivative of this indole (VIII) when oxidized with potassium permanganate produced inactive benzoylanthranilic acid (IX) thus showing that the radioactivity of the indole nucleus resided entirely in C_2. The radioactive carbon dioxide indicated that the C_β-activity of the tryptophan was to be found in the methylene carbon of the gramine side chain. Degradation of gramine to active 3-ethoxymethylindole and inactive ethyldimethylamine proved that no radioactive carbon was involved in the N-methyl groups. The conversion of 3-ethoxymethylindole (II) to 3,3′-di-indolylmethane (IV) by refluxing with aqueous sodium hydroxide was a convenient way of checking the activity in the 2-position and in the methylene group of the gramine since the product contained two indole nuclei and therefore two C_2 but only one methylene group. This self condensation of 3-ethoxymethylindole was expected since it had previously been discovered (10) that the related 3-hydroxymethylindole underwent the same condensation to 3,3′-di-indolylmethane.

The determination of the radioactivity of each of the degradation fragments (results shown in Table II) indicated that there had been no randomization of the activity in the gramine from feeding experiments (C), and that the ratio of activity in C_2 and C_β in the gramine was the same as in the administered tryptophan. It can therefore be concluded that tryptophan is indeed the precursor of gramine in sprouting barley and that the amino acid involved in the synthesis does not undergo scission to indole.

Although the activity of the gramine obtained from the initial experiment (B) was very low, it was possible to carry out the reaction with ethyl iodide

TABLE II
ACTIVITIES OF GRAMINE AND DEGRADATION PRODUCTS

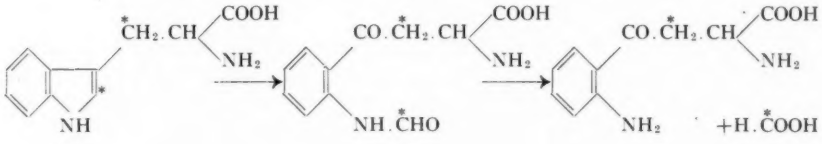
Experiment	Compound	Activity[3]	Labelled atoms
C	*dl*-Tryptophan fed		
	-2-C^{14}	1.68×10^7 disintegrations per min. (total activity) (1.0005 gm.)	C_2
	-β-C^{14}	1.91×10^7 disintegrations per min. (total activity) (0.0761 gm.)	$C\beta$
		$C_2/C\beta = 0.88$	
C	Gramine (I)	9.80×10^4 disintegrations per min. per millimole	$C_2 + C\beta$
	Gramine picrate	9.25×10^4 disintegrations per min. per millimole	$C_2 + C\beta$
	3-Ethoxymethylindole (II)	9.45×10^4 disintegrations per min. per millimole	$C_2 + C\beta$
	Ethyldimethylamine picrate (III)	0	—
	3,3′Di-indolylmethane (IV)	13.80×10^4 disintegrations per min. per millimole	$2C_2 + C\beta$
	Indole-3-carboxylic acid (V)	9.02×10^4 disintegrations per min. per millimole	$C_2 + C\beta$
	S-Benzyl-iso-thiouronium salt of (V)	9.56×10^4 disintegrations per min. per millimole	$C_2 + C\beta$
	Indole picrate (VI)	4.30×10^4 disintegrations per min. per millimole	C_2
	Barium carbonate (VII)	4.63×10^4 disintegrations per min. per millimole	$C\beta$
	N-Benzoylindole (VIII)	4.38×10^4 disintegrations per min. per millimole	C_2
	Benzoylanthranilic acid (IX)	0	—
	(IV)–(II)	4.35×10^4 disintegrations per min. per millimole	C_2
	2(II)–(IV)	5.10×10^4 disintegrations per min. per millimole	$C\beta$
	Mean value of C_2	4.34×10^4 disintegrations per min. per millimole	
	Mean value of $C\beta$	4.87×10^4 disintegrations per min. per millimole	
		$C_2/C\beta = 0.89$	

TABLE II (continued)

Experiment	Compound	Activity[3]	Labelled atoms
B	*dl*-Tryptophan fed		
	-2-C^{14}	1.71×10^7 disintegrations per min. (total activity) (1.0203 gm.)	C_2
	-β-C^{14}	3.96×10^7 disintegrations per min. (0.1562 gm.)	C_β
B	Gramine (I)	7.9×10^3 disintegrations per min. per millimole	
	3-Ethoxymethylindole (II)	4.8×10^3 disintegrations per min. per millimole	
	Ethyldimethylamine picrate (III)	3.1×10^3 disintegrations per min. per millimole	

[3] *All specific activities are for carrier free material and were determined on thin samples, making the usual corrections for self absorption, etc.*

and potassium ethoxide (11) to give 3-ethoxymethylindole and ethyldimethylamine isolated as the picrate. The results shown in Table II indicate that the N-methyl groups in this gramine were appreciably active. From what is known about the methylation of alkaloids in plants (4, 6, 8, 12, 14) this would seem to indicate that radioactive formate or other one-carbon compound has been produced in some way. In the feeding experiment (B) the high temperature and humidity in the germination cabinet produced considerable mold on the roots of the germinating barley and it is very probable that the mold degraded some of the radioactive tryptophan to formyl kynurenine (X) which would serve as a source of radioactive formate (cf. 5 for review of this degradation). Work is at present being carried out in order to determine whether formate is utilized by the sprouting barley for the production of the N-methyl groups of



X

gramine. In the feeding experiments (C) the seeds were dusted with a mercury fungicide which delayed the formation of mold on the seed envelopes.

EXPERIMENTAL[4]

Indole-2-C^{14}

C^{14}-Sodium formate (total activity 2.75×10^8 disintegrations per min., 4.92 mgm.) was shaken in a 50 ml. flask with *o*-toluidine hydrochloride (10.0

[4] *All melting points are corrected.*

mgm.) and freshly distilled *o*-toluidine (2.40 gm., 2.22 millimoles) on a steam bath. After about one minute, inactive 99% formic acid (0.92 gm., 2.00 millimoles) was added and the mixture heated at 100° in an atmosphere of dry nitrogen for 12 hr. The amber colored liquid was then cooled and treated with 1% hydrochloric acid which caused the crystallization of formyl-*o*-toluidine. It was washed with water and dried *in vacuo* (2.2225 gm., yield 82.5%). Potassium (1.1 gm.) was added to tertiary butyl alcohol (20 ml.) in a 3-necked 100 ml. flask and the mixture warmed in an atmosphere of dry nitrogen until the potassium had all dissolved. The formyl-*o*-toluidine was then added and the excess tertiary butyl alcohol distilled off and the residue heated slowly in a metal bath to 350–360°. After 15 min. all effervescence had ceased and the reaction mixture was cooled. Water was added and steam passed in to steam distil the indole-2-C^{14} which was collected in a cooled receiver as silvery white leaflets (0.6081 gm., yield 31.4%). It had a specific activity of 1.37×10^7 disintegrations per minute per millimole.

Degradation of Indole-2-C^{14}

A small quantity of active indole was diluted with inactive indole (2.0 gm.) to give a sample with a specific activity of 2.30×10^5 disintegrations per minute per millimole. This sample was dissolved in dry 1-methylnaphthalene (20 ml.) and sodium (0.8 gm.) was added to the solution which was stirred in an atmosphere of dry nitrogen for five hours at 190–200° (metal bath). The mixture was allowed to cool and the brown sodio-indole filtered off and washed with dry benzene. The sodio-indole was then suspended in dry cooled benzene (20 ml.) and benzoyl chloride (2.0 ml.) added to the suspension which was refluxed for two hours. The resulting pale brown solution was filtered and methanol added to the filtrate to destroy the excess benzoyl chloride. The solution was distilled under diminished pressure and the fraction, b.p. 200–230° at 20 mm., collected (1.30 gm.). This fraction, a pale yellow viscous oil, was dissolved in an equal volume of ethanol and the resulting solution on cooling deposited N-benzoylindole as colorless microscopic prisms, m.p. 66–68° (0.580 gm.). The literature records m.p. 67–68° (20). It had a specific activity of 2.23×10^5 disintegrations per minute per millimole.

This N-benzoylindole (0.400 gm.) was dissolved in acetone (50 ml.) and finely powdered potassium permanganate (1.00 gm.) was added to the stirred solution at room temperature. After five hours the acetone was removed *in vacuo* and the residue dissolved in warm water, the solution filtered, and the pale yellow filtrate treated with hydrochloric acid when a white precipitate of benzoylanthranilic acid was obtained. Crystallization from aqueous ethanol gave fine colorless needles, m.p. 181–182° (0.086 gm.), not depressed by admixture with authentic benzoylanthranilic acid obtained from anthranilic acid and benzoyl chloride. On assay for radioactivity it was found to be completely inactive.

dl-Tryptophan-2-C^{14} and dl-Tryptophan-β-C^{14}

These labelled amino acids were obtained by known methods for the synthesis of tryptophan on a small scale (1, 7, 13). Use of indole-2-C^{14} in the syn-

thesis gave tryptophan-2-C^{14} while C^{14}-formaldehyde gave tryptophan-β-C^{14} (2).

Growth of the Barley and Administration of the Tracer

In each of the feeding experiments (B) and (C) 720 gm. of barley (Charlottetown No. 80) was grown as previously described (2). In experiment C the barley seeds were dusted with a commercial fungicide, Semesan (manufactured by Bayer Co. Inc., New York), the active principle of which is hydroxymercurichlorophenol. This delayed the formation of mold on the seed envelopes. Before administering the tracer, the germinating barley which was matted together at the roots was taken out of the glass tray in which it was growing, shaken slightly to remove ungerminated barley seeds, and then placed in a clean tray containing a solution of the radioactive tryptophan. Details of the quantities of tryptophan fed to the plant are given in Table II. The procedure was to dissolve the active tryptophans in separate solutions, assay them, and then mix them in order to obtain accurately the ratio between the activities in the 2- and β-positions of the tryptophan actually fed to the barley[5]. The tryptophan (as the acetate with one molecule of acetic acid of crystallization) was fed to the barley as a solution in 600 ml. of distilled water.

Isolation of the Gramine from the Plant

The gramine was isolated from the dried leaves as previously described (2), and the weights and activities of the various fractions are summarized in Table III.

TABLE III
WEIGHTS AND ACTIVITIES OF EXTRACTS

Fraction (from 720 gm. of barley)	Experiment B		Experiment C	
	Wt., gm.	Activity, disintegration per min. per mgm.	Wt., gm.	Activity, disintegration per min. per mgm.
Dried leaves	68.8	—	54.6	—
Methanol extract of leaves	26.2	3.8	23.0	35
Crude gramine	0.3925	18.6	0.3293	425
Gramine (distilled and crystallized from benzene)	0.1721	45	0.1276	563

Degradation of the Gramine from the Plant

The number of degradations that could be carried out with the gramine from experiment B was limited by the low activity and the alkaloid was not

[5] *It was deemed advisable to use a mixture of tryptophan labelled in the 2-position and tryptophan labelled in the β-position rather than tryptophan-2-β-C^{14}. In such a mixture the ratio of C^{14} in the 2-position to C^{14} in the β-position is much more accurately known than the same ratio in the doubly labelled tryptophan-2-β-C^{14}.*

diluted. It was degraded to 3-ethoxymethylindole and ethyldimethylamine according to known procedures (2) (see Table II). The gramine from experiment C was diluted with 0.400 gm. of inactive gramine and degradations were carried out with this material.

(a) *Self Condensation of 3-Ethoxymethylindole*

3-Ethoxymethylindole (0.100 gm.) obtained from the gramine as described previously (2) was refluxed with 10% sodium hydroxide (20 ml.) for one hour. After cooling, the reaction mixture was filtered and the insoluble material crystallized from benzene. The product consisted of small colorless prisms, m.p. 161–162° (0.055 gm.) not depressed in admixture with 3,3′-di-indolylmethane (10).

(b) *Degradation to N-Benzoylanthranilic Acid*

The gramine was fused with potassium hydroxide as previously described (2) and the indolyl-3-carboxylic (m.p. 209°, S-benzyl-iso-thiouronium salt, m.p. 157.5°) decarboxylated to indole which was converted to the picrate (m.p. 187°, undepressed in admixture with an authentic specimen) and carbon dioxide which was absorbed in barium hydroxide. The indole recovered from the picrate was converted to N-benzoylindole and oxidized to benzoylanthranilic acid as described above. Whereas both the indole and barium carbonate were active, the last product was inactive showing that all the activity in the indole nucleus resided in the 2-position.

ACKNOWLEDGMENT

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BETATRON IRRADIATION OF AQUEOUS CERIC SULPHATE SOLUTION[1]

By R. W. Hummel[2], A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

Ceric ions, from ceric ammonium sulphate dissolved in aerated 0.8 *N* sulphuric acid solution, are reduced by Co^{60} γ-rays and betatron X-rays of 23 Mev. peak energy. *G* values were calculated on the basis of calculated electron distributions.

INTRODUCTION

Solutions of ceric ammonium sulphate in 0.8 *N* sulphuric acid have been recommended as chemical dosimeters for ionizing radiations (18), in particular for radiations of high intensity. In such cases the ferrous sulphate dosimeter is unsuitable owing to the decreased rate of ferrous ion oxidation after the oxygen concentration of the solution has been depleted (about 60 kiloroentgens). For ceric sulphate solutions the *G* value (the number of ceric ions reduced per 100 ev. absorbed) is independent of the oxygen concentration and of the rate of energy absorption from 0.37 to 2170 kiloroentgens per hour (8). The yield appears to be energy dependent at X-ray energies below about 300 KVP, but is energy independent from there up to the energy of Co^{60} γ-rays (9). The energy dependence at low energies has been related (9) to an increased specific ionization per unit of energy dissipated by secondary electrons.

The present investigation was carried out to study the usefulness of the system for chemical dosimetry and to extend the maximum of the energy range over which it has been studied.

EXPERIMENTAL PROCEDURE

Ceric ammonium sulphate (G. Frederick Smith) was dissolved in 0.8 *N* sulphuric acid to make an approximately 1.9×10^{-4} *M* solution. (It has been shown (8) that the yield is independent of concentration from 10^{-2} *M* to 2×10^{-5} *M*). The water was prepared by distilling tap water, first in an all-Pyrex apparatus from alkaline permanganate solution, then in an all-Pyrex apparatus from alkaline manganous hydroxide suspension, and finally from a Pyrex still into a silica condenser and receiver. The c.p. sulphuric acid was distilled from a dichromate solution (1). Fresh ceric ion solutions were prepared for each run the day before they were to be used. All glassware was Pyrex and was cleaned before use with hot chromic acid solution, followed by multiple rinses with tap water and triple-distilled water. In order to forestall any erratic results due to chemical effects by the radiations on untreated tubes, and also as an aid in removing oxidizable impurities, the tubes used for the irradiations were, in addition, filled with distilled water the day before use and placed around a 1-curie Co^{60} source in a lead castle. After removal from the castle they were cleaned with hot chromic acid solution, rinsed, and dried in an air

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oven. For irradiations with Co^{60} γ-rays, 3-ml. aliquots of ceric ion solution were used; for irradiations with betatron X-rays, 2-ml. aliquots were used.

Optical density measurements were made on a Beckman Model DU spectrophotometer, using silica cells and a hydrogen lamp. The molar extinction coefficient of ceric ammonium sulphate in 0.8 *N* sulphuric acid at 3300 Å was found to be 5314 ± 22, where the latter figure is the standard deviation. Measurement of the ceric ion concentration prior to an extinction coefficient determination was carried out by adding varying aliquots of ceric ammonium sulphate solution to constant aliquots of a ferrous sulphate solution and finding the optical density at 3040 Å where only ferric ions absorb. The molar extinction coefficient for ferric ion in 0.8 *N* sulphuric acid at $24 \pm 2°C.$ was 2213 ± 9. This was checked by irradiating a ferrous ammonium sulphate solution to complete oxidation, determining the ferric ion concentration using the coefficient, and comparing it with the initial ferrous ion concentration found using orthophenanthroline (extinction coefficient 11550 ± 30 at 5100 Å). The difference was less than 1%.

The optical densities of irradiated ceric ion solutions were found using the original solution as the 'blank'. For ferric ion measurements 0.8 *N* sulphuric acid was the blank.

Irradiations with the 1-curie Co^{60} source were carried out in a lead castle. The source could be withdrawn into the top of the castle so that the samples, in 13×100 mm. Pyrex tubes, could be inserted. The tubes were placed in holes in a ring-shaped Lucite block. The block was located on a brass disc, short pegs on the disc coinciding with small holes in the bottom of the block. A shallow brass cup was soldered onto the center of the disc. After inserting the Lucite–brass assembly an aluminum source-holder could be lowered to fit snugly into the brass cup. The Co^{60} was then above the rim of the cup with its center at the same height above the disc as the centers of the 3-ml. aliquots of solution. The details are shown in Fig. 1. Two Lucite blocks with different radii permitted measurements at dose rates of about 1.05 and 0.3 kiloroentgens per hour. Dose rates were determined initially with a Victoreen thimble chamber modified by replacing the Bakelite thimble by a Lucite thimble whose outer dimensions corresponded to 3.0 ml. of solution in a 13×100 mm. tube, and by replacing the central aluminum electrode by a longer one. This chamber was calibrated against recently calibrated* 25 r. and 100 r. Victoreen chambers using a 1100-curie Co^{60} source with about 3 m. between source and chamber. Irradiation of ferrous ammonium sulphate solutions using the 1100-curie and 1-curie sources and the 100 r. Victoreen and modified Victoreen, respectively, gave the same *G* values. Thus, the geometry of the modified Victoreen appeared to be such as to give reasonably accurate dose rate values at 3 cm. from the 1-curie Co^{60} source. Subsequent dose rate calculations were made using the decay constant for Co^{60}.

Irradiations with betatron X-rays were carried out in a rotating Lucite block described previously (12). A 100 r. Victoreen thimble chamber was used for dosimetry.

**Calibrations were checked at the National Research Council, Ottawa.*

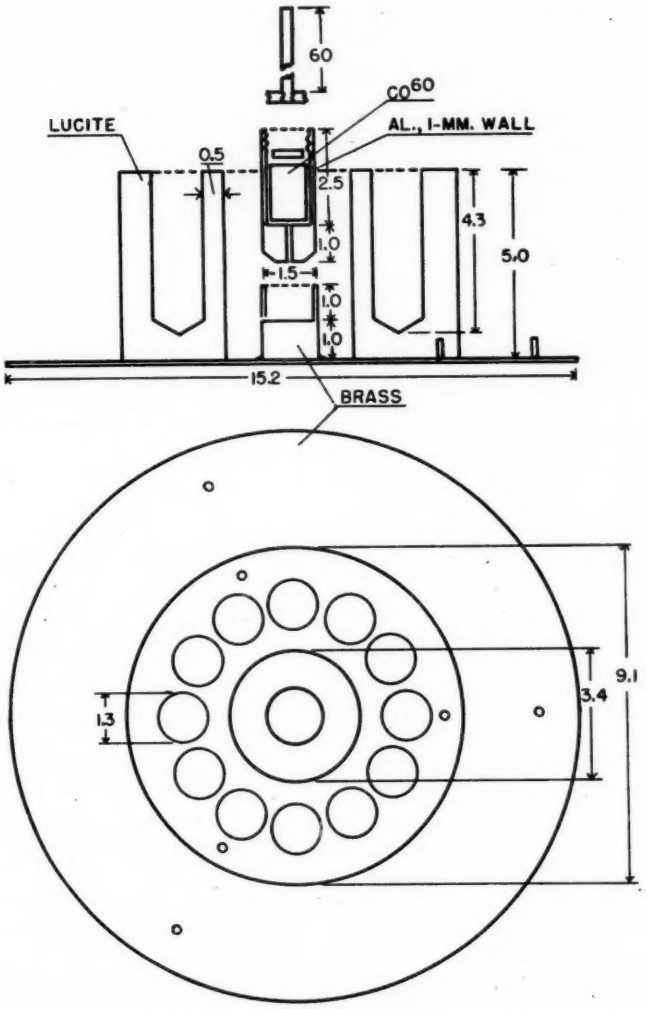

FIG. 1. Lucite block for irradiation with 1 curie Co^{60} source (dimensions in cm.).

The construction of the Lucite block was such that the minimum thicknesses of Lucite between ionization chamber (or solution) and X-ray source were, for the outer and inner circles of holes, 1.5 and 3.0 cm., respectively. These thicknesses give about 75% and 92%, respectively, of the ionization obtained with the equilibrium thickness (about 4 cm.). Thus for part of the time electronic equilibrium did not exist at the points of measurement. However, experiments with ferrous sulphate solutions, in which the results obtained in the inner and outer circles were compared (12), indicated that the intermittent

departure from electronic equilibrium was not of sufficient magnitude to be detectable by the techniques employed.

ENERGY ABSORPTION CALCULATIONS

The energy absorbed per unit volume of a medium irradiated with X- or γ-rays has often been calculated from an expression due to Bragg (2) and Gray (6), which is: $E_v = J.W.\rho$

where E_v = energy absorbed per unit volume of medium,

J = ion pairs produced per unit volume in an "infinitesimal" air cavity in the medium,

W = energy expended in producing an ion pair in air,

ρ = ratio of stopping powers, of medium with respect to air, for electrons.

The factors W and ρ are usually considered to be energy independent.

In this treatment W will be taken as 32.5 ev. (6) and ρ will be taken as a function of energy, weighted according to a calculated distribution of primary electrons in the medium, so that

$$[1] \qquad E_v = J.W.\frac{n_z}{n_a}.\frac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}$$

where n_z = electron density in the medium, in electrons per cm.^{3},

n_a = electron density in air, in electrons per cm.^{3},

${}_eS_z^c(E)$ = stopping power of medium with respect to collisional energy losses by primary electrons, per electron of medium, at primary electron energy E in Mev. cm.^{2} per electron,

${}_eS_a^c(E)$ = same as ${}_eS_z^c(E)$, but for air,

$N_z(E)$ = number of primary electrons, with energies in a small interval about E, at a point in the medium.

Stopping powers were calculated from the Bethe-Bloch expression for the rate of energy loss by collisions by electrons passing through a medium. Account was also taken of the polarization properties of a medium, whereby the rate of energy loss by collisions is decreased, by multiplying the stopping powers of 0.8 N sulphuric acid, calculated from the Bethe-Bloch equation, by the ratio of the modified stopping power of water to the unmodified value, at various energies, as taken from Fig. 3 of a paper by Halpern and Hall (7). The stopping powers of air were calculated from the Bethe-Bloch equation. There is no polarization effect in air at these energies.

The average excitation potential $\bar{I}$, which appears in the Bethe-Bloch equation, was taken as 45 ev. in 0.8 N sulphuric acid and 97.6 ev. in air. The former value is the mean of two recent determinations, as quoted by Platzman (17). The latter was calculated as follows:

$$\bar{I} = k\bar{Z} = 13.5\bar{Z} \text{ ev.},$$

where $\bar{Z}$ is given by

$$\ln \bar{Z} = a_1 \ln Z_1 + a_2 \ln Z_2 + \ldots$$

where a_1, a_2, etc., are the fractions of the total number of electrons which belong to atoms with atomic numbers Z_1, Z_2, etc.

For Co^{60} γ-rays the number of primary electrons produced per unit energy interval per electron of material per photon per cm.^{2} was calculated using the differential Klein-Nishina coefficient and the method given by Johns *et al.* (13). The number existing per unit volume at a given instant was obtained by multiplying by the electron density, and adding to those produced in a given energy interval the number degraded from high energy intervals. The number of primary electrons in a given energy interval occurring at a point in the medium was assumed proportional to the distance travelled by the electrons as they were degraded through that energy interval. These distances, ΔR, were calculated by plotting the reciprocal of the total rate of energy loss, $(-dE/dx)^t$, in Mev. per cm., against the energy, E. The total rate of energy loss is the sum of the collisional and radiational losses, i.e.,

$$\left(-\frac{dE}{dx}\right)^t = \left(-\frac{dE}{dx}\right)^c + \left(-\frac{dE}{dx}\right)^r.$$

The collisional contribution was calculated from the Bethe-Bloch equation, modified as required by the polarization factors, while the radiational contribution was obtained from expressions given by Heitler (10). The range, ΔR, was the area under the curve between the energies involved. For Co^{60} radiations the energy interval was 0.1 Mev. while for betatron radiations the interval taken was 1 Mev.

For betatron X-rays of 24 Mev. peak energy, the number of primary electrons produced per cm.^{3} of water per photon per cm.^{2} for a range of initial electron energies and for photon energies from 0–25 Mev. have been tabulated by Cormack and Johns (4, Tables I and III). To find the number of primary electrons produced by the Compton process in a cm.^{3} of 0.8 N sulphuric acid, the values for water were multiplied by the ratio of electron densities. To find the number produced by the pair process in this material, the values for water were multiplied by the ratios of effective atomic numbers and electron densities. The effective atomic number of a material, for the pair production process, is found from the equation:

$$Z_{\text{eff.}} = a_1Z_1 + a_2Z_2 + \ldots + a_nZ_n,$$

where a_1 and Z_1, etc., have the same meanings as before. The numbers of Compton and pair electrons so obtained were on the basis of one photon per cm^2. They were multiplied by the photon flux obtained from Fig. 3 of a paper by Johns *et al.* (14), by dividing the values of the ordinates of the modified Schiff curve, in ergs per cm.^{2}, at given photon energies, by the photon energies. Tables were constructed giving the relative number of electrons produced per Mev. interval per cm.^{3} of material at various photon energies. The relative numbers of electrons existing in any energy interval were then obtained by adding the contributions due to the various photon energies. The relative numbers of primary electrons occurring at a point were obtained as described above in the case of Co^{60} radiations.

Having calculated ${}_eS^c(E)$ and $N_z(E)$ at all electron energies, the ratio in equation [1] could be calculated. It should be noted that $N_z(E)$ is the number of electrons in an energy interval, that ΔR is the range in that interval, and that ${}_eS^c(E)$ is taken at the middle of the interval.

The results of the calculations are given in Table I, where B.–B. refers to calculations based on the Bethe-Bloch equation, and H.-H. refers to those calculations modified by the factors taken from Halpern and Hall.

TABLE I
RESULTS OF ENERGY ABSORPTION CALCULATIONS

Radiation source	Basis of calculation	$\dfrac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}$	Relationship between energy absorption and Victoreen reading
Cobalt	B.-B.	1.092	$E_v = 6.50 \times 10^{13}\cdot V_r$
Betatron	B.-B.	1.075	$E_v = 6.40 \times 10^{13}\cdot V_r$
	H.-H.	1.042	$E_v = 6.20 \times 10^{13}\cdot V_r$

The relationships in Column 3 of Table I were obtained by taking $J = 2.082 \times 10^9$ ion pairs/cm.^{3}/r. $\times V_r$, where V_r is the Victoreen meter reading in r. (roentgens), corrected for temperature and pressure, so that Equation [1] becomes:

$$E_v = 2.082 \times 10^9 \cdot V_r \cdot 32.5 \cdot \frac{3.42 \times 10^{23}}{3.888 \times 10^{20}} \cdot \frac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}$$

$$= 5.952 \times 10^{13} \cdot V_r \cdot \frac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}.$$

RESULTS

The results of irradiations of 1.9×10^{-4} M ceric ammonium sulphate solutions are given in Table II. Values of G, the number of ceric ions reduced per 100 ev. absorbed in the solution, are given on the basis of the two sets of calculations described above. Yields are also given in terms of the number of micromoles reduced per liter of solution per kiloroentgen as measured with the Victoreen.

Application of the equations in Table I to experimental results obtained with ferrous ammonium sulphate solutions in 0.8 N sulphuric acid gave, for Co^{60} γ-rays, $G(Fe) = 15.8 \pm 0.2$, and for betatron X-rays $G(Fe) = 15.5 \pm 0.4$ (B.-B.) or 15.9 ± 0.4 (H.-H.). The ratios of these results to the results of ceric solution irradiations are given in Table III, together with recent results reported in the literature.

The deviations from the means in Table II and III are, for the present work, in terms of the standard deviations, $(\sigma)(n - 1$ degrees of freedom). The devi-

TABLE II
RESULTS OF IRRADIATIONS OF CERIC AMMONIUM SULPHATE SOLUTIONS

Radiation	Expt. No.	Yield G B.-B.	Yield G H.-H.	Yield $\mu M./l./1000 V_r$.
Co^{60} γ-rays	1	2.65	—	2.86
	2	2.70	—	2.92
	3	2.60	—	2.82
	4	2.66	—	2.87
	Mean	2.65 ± 0.04	—	
Betatron X-rays	1	2.69	2.77	2.84
	2	2.51	2.59	2.67
	3	2.50	2.58	2.66
	4	2.49	2.57	2.65
	Mean	2.55 ± 0.09	2.63 ± 0.09	

TABLE III
RATIOS OF RESULTS WITH FERROUS AND CERIC SOLUTIONS

	$G(Fe)/G(Ce)$*
Present work, Co^{60}	$15.8 \pm 0.2/2.65 \pm 0.04 = 5.96 \pm 0.12$
Present work, betatron (B.-B.)	$15.5 \pm 0.4/2.55 \pm 0.09 = 6.08 \pm 0.27$
Present work, betatron (H.-H.)	$15.9 \pm 0.4/2.63 \pm 0.09 = 6.05 \pm 0.25$
Hardwick (8), Co^{60}	$20.8 \pm 0.3/3.30 \pm 0.03 = 6.30 \pm 0.11$
Hochanadel and Ghormley (11), Co^{60}	$15.6 \pm 0.3/2.52 \pm 0.05 = 6.19 \pm 0.17$
Weiss (18)	5.96 ± 0.03

**All G values in Table III were calculated on the basis of 32.5 ev. expended per ion pair formed in air except those of Hardwick which were based on 31.9 ev.*

ations of the G value ratios, except for Weiss's, were obtained from the expression (5):

$$\rho = \pm 1/G(Ce) \sqrt{\sigma^2(Fe) + \left\{\frac{G(Fe) \cdot \sigma(Ce)}{G(Ce)}\right\}^2}.$$

DISCUSSION

Ceric ammonium sulphate solutions are not suitable as dosimeters for low intensity γ-ray and X-ray beams owing to the relatively low yield. For beams of high intensity the low yield may be an advantage, but this has to be balanced against the precautions which must be taken if consistent results are to be obtained. The details concerning the preparation of ceric sulphate solutions as given under *Experimental Procedure* are only an indication of the difficulties involved. Miller and Wilkinson (16) have commented recently on this disadvantage.

Application of the "Student's t" test (19) to the mean values given in Table II shows that, based only on the Bethe-Bloch equation, the means obtained with Co^{60} and betatron radiations are not significantly different at the 95% level of significance (6 degrees of freedom), and that the means based on application of the correction factors from Halpern and Hall are essentially the same.

It may, therefore, be inferred that energy yields (G) for ceric sulphate in 0.8 N sulphuric acid solutions are energy-independent in the range covered, and that the pulsed nature of the betatron beam (a 4 μsec. pulse 180 times per second) is not an important factor.

It should be kept in mind that the calculations carried out here are based on the primary electron distribution in 0.8 N sulphuric acid and on the distribution in an infinitesimal air cavity in the solution such that the distribution is unaltered. Actually, the ionization measurements were done with Victoreen thimble chambers. Experiments reported elsewhere (3) indicate that the error involved probably does not exceed 2 or 3%. Our results (Table III) are therefore much more in accord with those of Hochanadel and Ghormley (11), $G(\text{Fe}) = 15.6$, $G(\text{Ce}) = 2.52$, than with those of Miller (15), $G(\text{Fe}) = 20.3$, and Hardwick (8), $G(\text{Fe}) = 20.4$, $G(\text{Ce}) = 3.2$. All these G values are based on 32.5 ev. expended per ion pair formed in air.

ACKNOWLEDGMENT

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THE STRUCTURE AND GRIGNARD REACTION OF THE β-AMINOCROTONONITRILE[1]

By Jaspar J. Conn[2] and Alfred Taurins

ABSTRACT

The ultraviolet absorption spectra of the low and high melting forms of β-aminocrotononitrile (I) provide evidence that both of them possess the same enamine structure. Since the existence of the polymorphic modifications of I must be excluded on the basis of the thermochemical behavior of I, the difference of the two modifications is capable of accounting for *cis* and *trans* isomerism, the low melting modification being the *cis* form, and the high melting modification being the *trans* form.

In the reaction of I with aromatic Grignard reagents β-amino ketones of the type $CH_3-CO-CH=C(NH_2)-R$ are formed as the main reaction products.

The free radical mechanism of the formation of I is postulated.

INTRODUCTION

The treatment of acetonitrile (3) and propionitrile (7) with sodium in the absence of a solvent gives aminopyrimidine derivatives. However, in benzene solution sodium produces with acetonitrile the β-aminocrotononitrile (I) (9), and propionitrile gives 3-amino-2-methyl-2-pentenenitrile (II) (10, 11). The same type of condensation occurs between acetonitrile and aromatic nitriles (11, 13, 14, 16), or higher aliphatic nitriles (15, 18).

von Meyer (13) obtained I in the form of two crystalline modifications: the low melting (52–53°) modification having the higher solubility in benzene, and the high melting (79–83°) modification having the lower solubility in benzene. von Meyer postulated the ketimine–enamine tautomerism of this substance. However, he did not give any proof of this idea. Although I is a versatile reagent in organic synthesis, the structure of the two modifications of I is not known as yet.

The objective of this work was twofold: firstly, to study the properties of I to elucidate the nature of the two modifications, and secondly, to find out whether the Grignard reaction of I could serve as a preparative method for the synthesis of β-amino ketones.

DISCUSSION

Mechanism of Formation

The chemical equations of the formation of I from acetonitrile and sodium, as they were given by von Meyer (10) and Holtzwart (9) did not represent a detailed mechanism of the reaction. Therefore we propose a new mechanism of formation of β-aminocrotononitrile involving free radical intermediates (Chart I). In the primary interaction a free methyl radical is formed. The free methyl radical extracts a hydrogen atom from the second molecule of aceto-

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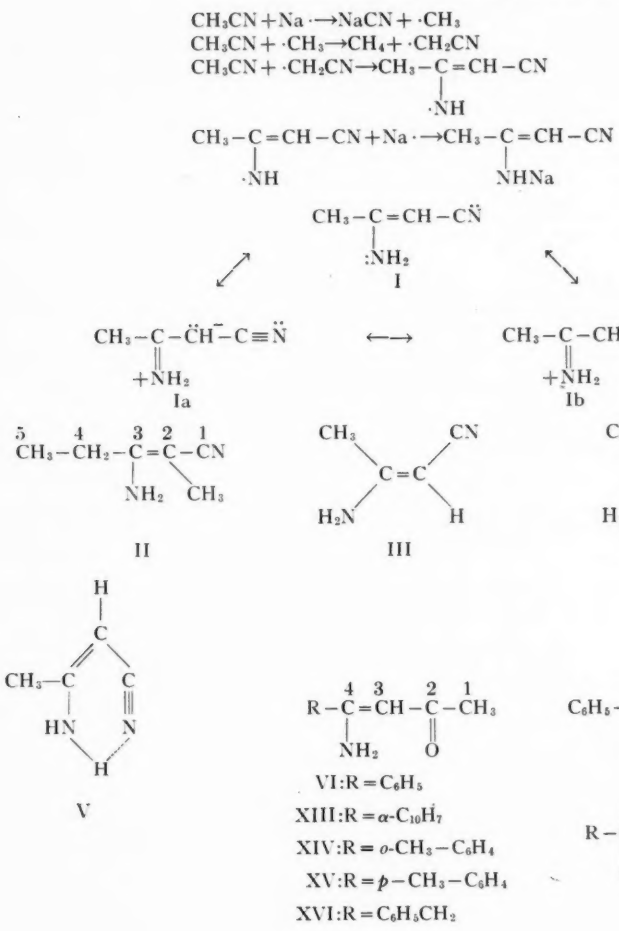
[2] *Holder of a National Research Council Fellowship 1950–1951.*

CHART I

FREE RADICAL MECHANISM OF FORMATION OF I



nitrile, forming methane and the free $\cdot CH_2CN$ radical. This radical attacks the third molecule of acetonitrile to form the free β-aminocrotononitrile radical, which reacts with the second atom of sodium to produce the sodium salt of β-aminocrotononitrile. This mechanism could apply equally well to the reaction of other aliphatic nitriles with sodium in benzene solution.

The Ultraviolet Absorption

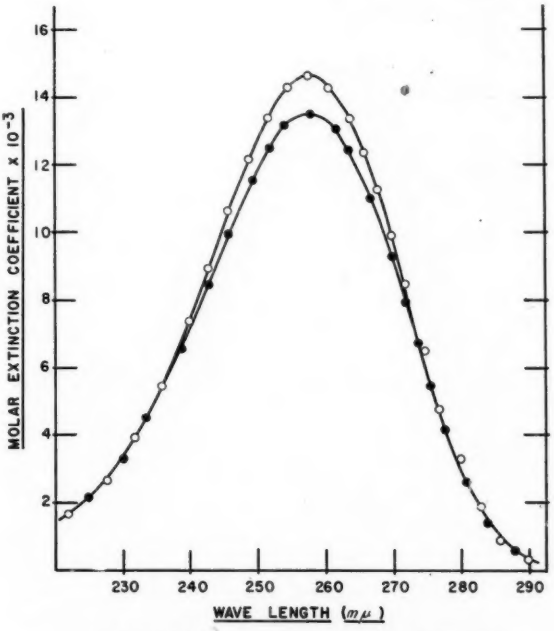
The ultraviolet absorption spectra of both the modifications of I were determined in absolute ethanol and acetonitrile in the region from 220 to 295 mμ. In both solvents, the absorption curves were symmetrical with only

one well defined maximum at almost the same wave length for both modifications (Table I), (Figs. 1 and 2).

The observed ultraviolet absorption indicates that both the modifications of I have identical electronic configuration when dissolved in polar solvents, and therefore the existence of the tautomeric forms of I must be excluded. The spectra are in accordance with the enamine structure of I, in which the

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA OF β-AMINOCROTONONITRILE

	Absolute ethanol		Acetonitrile	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
Low melting modification	258 mμ	13600	254.5 mμ	12430
High melting modification	256 mμ	14700	254.5 mμ	13650



ULTRAVIOLET ABSORPTION SPECTRA

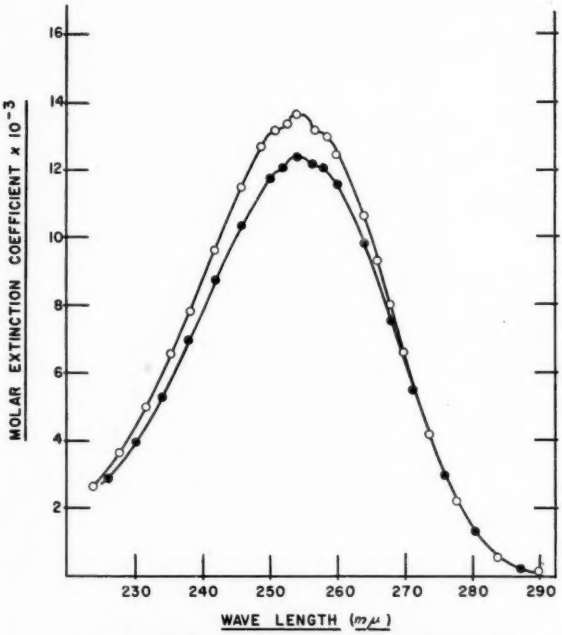
FIG.—1

○ HIGH MELTING β AMINOCROTONONITRILE

● LOW MELTING β AMINOCROTONONITRILE

CONCENTRATION.— 0.0001 MOLAR IN ABSOLUTE ETHANOL

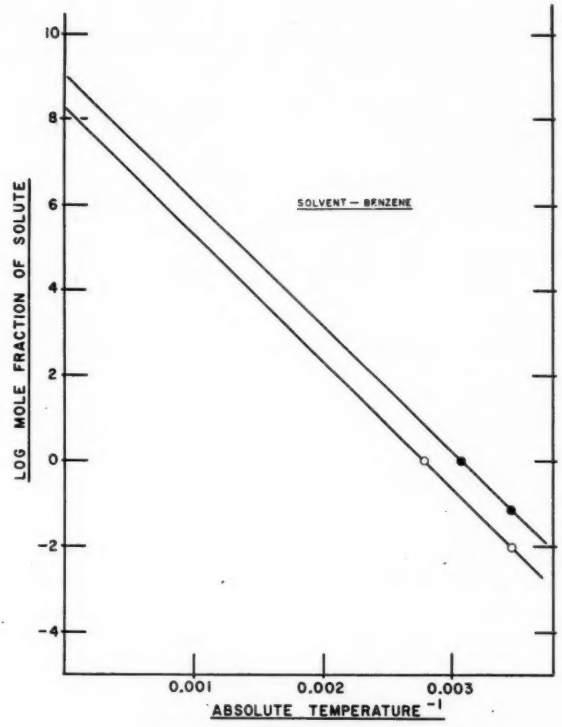
conjugation of the carbon–carbon double bond and cyano group, and the interaction of the amino group gives rise to the molar extinction coefficients and the shift of the λ_{max} towards the longer wave lengths, comparing the ultraviolet absorption of I with that of butyronitrile (λ_{max} 180 mμ) and acrylonitrile (λ_{max} 250 mμ) (4). The enamine form of I can exist as a resonance hybrid of three resonating structures I $\leftrightarrow$ I*a* $\leftrightarrow$ I*b*, two of them being ionic (I*a*, I*b*).



Heats of Melting and Solution

It is known that in an ideal solution, the heat of solution of a solid is identical with its heat of melting at the same temperature (17).

Rough values for the heats of melting of the two modifications of I are therefore given by the heats of solution of the two modifications in benzene, assuming ideal conditions for the solutions. Knowing the melting points of the two modifications, and their solubilities at 16.5°, it is possible to obtain the solubility curves for the two modifications. The plot of the mole fraction versus the inverse of the absolute temperature is a straight line (Fig. 3). The



SOLUBILITY RELATIONSHIP

FIG. 3

○ HIGH MELTING β AMINOCROTONONITRILE
● LOW MELTING β AMINOCROTONONITRILE

heats of solution are obtained by multiplying the intercept by the term 2.303 RT. It is found that the values of the heats of solution of the two modifications, at the melting point, are identical within experimental limits of error (Chart III). It is quite safe to assume that the heats of melting of the two modifications will be of the same order of magnitude, and almost identical to each other.

CHART III

CALCULATION OF HEATS OF SOLUTION AND HEATS OF FUSION OF β-AMINOCROTONONITRILE MODIFICATIONS

Data for solubility curves of benzene solutions of β-aminocrotononitrile

Low Melting Modification:

Solubility at 289.5°A. = 8.57 gm./100 gm. of benzene.
Mole fraction of solute = 0.0755.
Log mole fraction = −1.122.
Inverse of absolute temperature = 0.00346.

Melting point = 325°A.
Inverse of absolute temperature = 0.00308.
Log mole fraction = 0.0.

High Melting Modification:

Solubility at 289.5°A. = 1.22 gm./100 gm. of benzene.
Mole fraction of solute = 0.0115.
Log mole fraction = −1.939.
Inverse of absolute temperature = 0.00346.

Melting point = 352–357°A.
Inverse of absolute temperature = 0.00280.
Log mole fraction = 0.0.

Intercept for *High Melting Modification* = 9.10.
Heat of solution = 9.10 × 4.576 × 325 = 13,500 cal./mole.

Intercept for *Low Melting Modification* = 8.22.
Heat of solution = 8.22 × 4.576 × 357 = 13,600 cal./mole.

The heats of melting of enamine and ketimine tautomers would not be identical, with the result that such tautomers are ruled out as possible structures for the two modifications of I.

Polymorphic Modifications

The possibility of the two modifications of I being polymorphic modifications has been considered.

Enantiotropic polymorphism demands the existence of a transition temperature, above which one modification would be stable and the other modification would be reversed (8). That means that the two forms should be entirely interconvertible at some temperature below their melting points. Also, there should be only one melting point for the compound. No such transition temperature has been found for I, the lower melting modification being the stable modification at all temperatures. Both forms have definite melting points. These lines of evidence rule out the existence of enantiotropic polymorphism of I.

Monotropic polymorphism appears to be a likely possibility at first. Such polymorphism demands the existence of an imaginary transition temperature, that is, one which is above the melting points of the two modifications (8). One modification would be stable, and the other would be metastable at all times. There would be two melting points, one for each modification. Such stability and the two melting points were found in the case of I. However, the order of stability is the reverse of the expected one. The lower melting modification, if it is a polymorph of the monotropic type, should be the metastable form and should spontaneously transform into the higher melting modification. Investigation of the I has shown that the low melting modification is the more stable of the two modifications, and that the direction of transformation is from the high melting form to the low melting form. In addition, the heats of fusion of polymorphic modifications have been found to differ greatly. Because the heats of fusion of the two modifications of I were found to be nearly identical, the existence of monotropic polymorphism has been ruled out.

Cis and Trans Isomerism of I

Since the two possibilities to explain the existence of two modifications of I were excluded as a result of the present investigation, we propose that these

modifications are *cis* and *trans* isomers. The high melting form (79–83°) has been given the *trans* structure (III) by virtue of its higher melting point and lower solubility. The low melting form (52–53°) has been given the *cis* structure (IV) on the basis of its lower melting point and higher solubility. In the *cis* form, the amino and cyano groups are in adjacent positions, and can form an internal hydrogen bond (V), which would make the *cis* form more stable than the *trans* isomer. This means that irradiation of the lower melting form with ultraviolet light would not cause any transformation of the molecule into the higher melting form. The additional ionic structures I*a* and I*b* could influence the crystallization of I from organic solvents. From a nonpolar solvent, like benzene, both modifications can be easily crystallized without any changes. However, crystallization of these modifications from a polar solvent, like ethanol, produce only the low melting form. The explanation of this behavior is that in polar solvents, the contribution of the ionic structures I*a* and I*b* to the resonance hybrid would be greater than in a nonpolar solvent. The structures I*a* and I*b* do not possess the double bond of the enamine system, permitting the free rotation about the single bond between the α- and β-carbon atoms, and consequently, the change of the unstable modification into the stable one.

The Grignard Reaction

The Grignard reaction of I starts in the amino group by substituting both

GRIGNARD REACTION OF I

$$I + 2RMgX \rightarrow CH_3-\underset{\underset{N(MgX)_2}{|}}{C}=CH-C\equiv N + 2R-X$$

XXII

$$XXII + RMgX \rightarrow CH_3-\underset{\underset{N(MgX)_2}{|}}{C}=CH-\underset{\underset{R}{|}}{C}=N-MgX$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{NH}{\|}}{C}-R \quad \rightleftarrows \quad CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{R}{|}}{C}-NH_2$$

VI, XIII — XVI

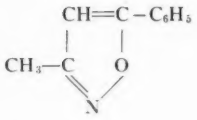
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-R$$

XX, XXI

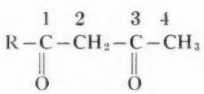
of the hydrogen atoms by the MgX groups and the formation of two hydrocarbon molecules (15). Only if the threefold excess of the Grignard reagent is used the nitrile group is also attacked. In the reaction of I with aromatic Grignard reagents substituted β-amino ketones (VI, XIII–XVI), and β-diketones were isolated as the final reaction products in varying yields.

Phenylmagnesium bromide and I gave the 4-amino-4-phenyl-3-butene-2-one (VI). The structure of VI was evidenced by the fact that it gave with hydroxylamine hydrochloride 3-methyl-5-phenylisoxazole (IX) (6). The latter

CHART II

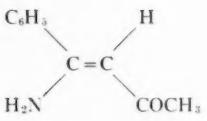


IX

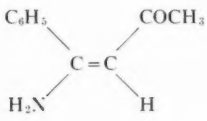


XX: R = C_6H_5

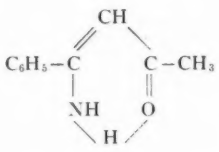
XXI: R = α-$C_{10}H_7$



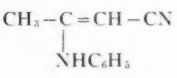
X



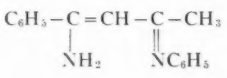
XI



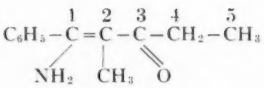
XII



XVII



XVIII



XIX

compound could only be formed if the N=OH group, and therefore the carbonyl group of the β-amino ketone, was adjacent to the methyl group. As further proof of the position of the carbonyl group in VI, the β-phenylaminocrotononitrile (XVII) was reacted with phenylmagnesium bromide. The main reaction product was 1-amino-1-phenyl-3-phenylimino-1-butene (XVIII) which on hydrolysis with 75% sulphuric acid produced 4-amino-4-phenyl-3-butene-2-one (VI).

The VI isolated in this investigation was an oil, boiling at 70–80° at 1 mm. of pressure. The boiling point of VI was not in agreement with physical properties of the two isomer amino ketones prepared by Claisen (5). The latter compounds were 4-amino-4-phenyl-3-butene-2-one, melting point 86–87°, and 3-amino-1-phenyl-2-butene-1-one, melting point 143° (VIII).

The fact that two compounds have been identified as having the structure VI is believed to be due to the *cis–trans* isomerism, as shown by the formulae X and XI. The amino ketone, boiling point 70–80° at 1 mm., is assumed to be the *cis* form, because it has the lower melting point of the two known isomers. The substance, isolated by Claisen (5), is given the *trans* configuration. The *cis* isomer can be stabilized by the hydrogen bond (XII), as in the case of the enol forms of β-diketones.

The presence of the carbon–carbon double bond and exclusion of other possible structures for the obtained substance VI is evident from the following

considerations. The failure of the VI to give a positive test with ferric chloride solution indicates that there is no enol formation. The β-ketimino ketone structure (VII) was also excluded, since this structure cannot form any resonance forms, contrary to β-amino ketone structure which is stabilized by resonating ionic forms (VI*a* and VI*b*).

In the reactions of aromatic Grignard reagents with I, 1-phenyl-1,3-butanedione (XX) and 1-α-naphthyl-1,3-butanedione (1) (XXI) were isolated in yields of 5–10%. It is evident that these β-diketones were formed by hydrolysis of the corresponding β-amino ketones, VI and XIII respectively.

The reaction of β-amino nitriles with Grignard reagents was extended to include the 3-amino-2-methyl-2-pentenenitrile (II). This substance gave with phenylmagnesium bromide 1-amino-2-methyl-1-phenylpentene-3-one (XIX).

EXPERIMENTAL*

Preparation of β-Aminocrotononitrile (I) (13).

The main feature of the preparation of the two modifications of I is the decomposition of the sodium salt of I with water at different temperatures. The low melting modification is obtained if the decomposition of the salt is carried out at 30°. The preparation of the high melting modification requires the use of ice-cold water. In both cases I is extracted from the reaction mixture with ether. After the evaporation of ether at reduced pressure the crystalline residues are recrystallized from benzene.

Since both modifications of I did not show any difference in reactions with other substances, the low melting modification was only used in the study of the Grignard reaction of I.

Ultraviolet Absorption Spectra

Ultraviolet absorption spectra were obtained using a Beckman quartz spectrophotometer model DU. The solvents, ethanol and acetonitrile, were purified by the standard methods.

Reaction of I with Phenylmagnesium Bromide

Ten grams (0.15 mole) of I dissolved in 100 ml. of ether were added with stirring to a solution of 0.5 mole of phenylmagnesium bromide in 300 ml. ether over a period of 10 min. A dark oil separated from solution. The mixture was then refluxed for six hours.

(*a*) *4-Amino-4-phenyl-3-butene-2-one* (VI)

The Grignard complex was decomposed by the gradual addition of an ice-cold saturated aqueous ammonium chloride solution. The ether layer was separated and the aqueous solution was extracted with ether. The combined ether extract was dried and distilled under reduced pressure to yield VI as a light colorless oil, boiling at 70–80° at 1 mm. pressure. The yield was 5.0 gm. (20%).

The 2,4-dinitrophenylhydrazone of VI, crystallized from benzene as orange needles, melting point 241–242°.

* Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Anal. calc. for $C_{16}H_{15}N_5O_4$: C, 56.30; H, 4.40; N, 20.53%. Found: C, 56.28; H, 4.29; N, 20.40%.

3-Methyl-5-phenylisoxazole (IX).—A mixture of 0.5 gm. of VI, 0.5 gm. of hydroxylamine hydrochloride, and 2.0 gm. of potassium hydroxide in 5 ml. of water were refluxed for two hours. The reaction product IX was recrystallized from alcohol as white needles, melting at 67°, lit. (6) m.p. 67–68°.

Anal. calc. for $C_{10}H_9NO$: N, 8.81%. Found: N, 8.70%.

(*b*) *1-Phenyl-1,3-butanedione* (XX)

(*α*).—Following decomposition of the Grignard complex and extraction with ether, the alkaline aqueous solution was neutralized with hydrochloric acid and cooled. A precipitate of XX was removed by filtration and recrystallized from ethanol as white needles, melting at 60–61°; lit. (6). The yield was 1 gm. (5%).

(*β*).—The ether solution of the decomposed Grignard complex was repeatedly extracted with 20 ml. portions of saturated sodium bicarbonate solution until the aqueous portion was colorless. The bicarbonate solution was acidified with hydrochloric acid, and cooled in ice. The crystalline precipitate was recrystallized from ethanol as white needles, m.p. 60–61°. The yield was 2.0 gm. (10%).

Reaction of hydroxylamine with XX.—The XX was treated with hydroxylamine hydrochloride in a procedure similar to that described previously, and IX was obtained as white needles, m.p. 66–67°.

Anal. calc. for $C_{10}H_9NO$: N, 8.81%. Found: N, 8.72%.

Reaction of I with α-Naphthylmagnesium Bromide

Ten grams (0.15 mole) of I and 0.5 mole of α-naphthylmagnesium bromide were reacted in a procedure similar to that described in the reaction of phenylmagnesium bromide. The residue which was obtained by the evaporation of the ether extract was steam-distilled to remove naphthalene produced by the reaction of the Grignard reagent with the active hydrogen of I. Following the steam distillation, the residue was extracted with ether.

(*a*) *4-Amino-4-α-naphthyl-3-butene-2-one* (XIII)

The dried ether extract was distilled under reduced pressure, yielding 6.5 gm. (25.2%) of a light oil, boiling at 130–135° at 1 mm.

Anal. calc. for $C_{14}H_{13}NO$: N, 6.48%. Found: N, 6.30%.

The 2,4-dinitrophenylhydrazone of XIII was recrystallized from benzene as fine orange needles, m.p. 216–217°.

Anal. calc. for $C_{20}H_{17}N_3O_4$: C, 61.38; H, 4.35; N, 17.90%. Found: C, 61.44; H, 4.14; N, 17.61%.

The semicarbazone of XIII had the m.p. 213–214° (white plates from ethanol).

Anal. calc. for $C_{15}H_{16}N_4O$: N, 20.90%. Found: N, 20.76%.

Reaction of hydroxylamine with XIII gave 3-methyl-5-α-naphthylisoxazole (IX) as white plates crystallized from ethanol, m.p. 140–141°.

Anal. calc. for $C_{14}H_{11}NO$: N, 6.70%. Found: 6.82%.

(*b*) *1-α-Naphthyl-1,3-butanedione* (XXI)

The ether extract of the decomposed Grignard complex was repeatedly extracted with saturated bicarbonate solution. The latter was neutralized with hydrochloric acid, and cooled. The precipitate was recrystallized from ethanol as fine prisms, melting at 107–108°. The yield was 1.5 gm. (5.8%).

Anal. calc. for $C_{14}H_{12}O_2$: C, 79.25; H, 5.66%. Found: C, 79.27; H, 5.60%.

4-Amino-4-o-tolyl-3-butene-2-one (XIV).—This substance was prepared from *o*-tolylmagnesium bromide and I. It was a light yellow oil, boiling at 40–50° at 4 mm. The yield was 2.5 gm. (11%).

The 2,4-dinitrophenylhydrazone of XIV, orange needles, melting at 162–163°.

Anal. calc. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.79; N, 19.72%. Found: C, 57.81; H, 4.25; N, 19.41%.

4-Amino-4-p-tolyl-3-butene-2-one (XV).—It was obtained in the reaction of *p*-tolylmagnesium bromide and I. XV was a yellow oil, distilling at 30–40° at 4 mm. The yield in several preparations varied from 2.5 to 3.2 gm. (11–15%).

The 2,4-dinitrophenylhydrazone of XV, fine red needles from benzene, m.p. 259–260°.

Anal. calc. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.79; N, 19.72%. Found: C, 57.62; H, 4.58; N, 19.65%.

4-Amino-5-phenyl-3-pentene-2-one (XVI).—This compound was synthesized from I and benzylmagnesium bromide. It was a yellow oil, distilling at 70–75° at 1 mm. The yield was 3.5 gm. (16%).

The 2,4-dinitrophenylhydrazone of XVI, orange needles from benzene, m.p. 146–147°.

Anal. calc. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.79; N, 19.72%. Found: C, 57.53; H, 4.78; N, 19.62%.

1-Amino-1-phenyl-3-phenylimino-1-butene (XVIII).—The reaction between 19.2 gm. of XVII and 0.75 mole of phenylmagnesium bromide in 400 ml. ether was carried out for 48 hr. The reaction mixture was decomposed with ammonium chloride solution and extracted with ether. After evaporation of ether the residue was distilled under reduced pressure. The first fraction, boiling at 50–80° at 3 mm., was aniline (3.5 gm.). Distillation was stopped at this point, and the residue was crystallized from alcohol. The XVIII formed yellow crystals, m.p. 85–86°. The yield was 6.5 gm. (12%).

Anal. calc. for $C_{16}H_{16}N_2$: C, 81.36; H, 6.78; N, 11.86%. Found: C, 81.59; H, 6.70; N, 11.75%.

Acid hydrolysis of XVIII with 75% sulphuric acid at 150–160° for one hour yielded VI, which was identified by its 2,4-dinitrophenylhydrazone, m.p. 241–242°. The hydrazone was also analyzed quantitatively.

Anal calc. for $C_{16}H_{15}N_5O_4$: C, 56.30; H, 4.40; N, 20.53%. Found: C, 56.22; H, 4.16; N, 20.26%.

1-Amino-2-methyl-1-phenyl-1-pentene-3-one (XIX).—In the reaction between 20.7 gm. of II and 0.6 mole of phenylmagnesium bromide in 400 ml. ether, 5.2 gm. (15%) of XIX was obtained as a light oil distilling at 80–90° at 8 mm.

The 2,4-dinitrophenylhydrazone of XIX was crystallized from benzene as bright orange needles, m.p. 230–231°.

Anal. calc. for $C_{18}H_{19}N_5O_4$: N, 18.97%. Found: N, 18.68%.

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INFRARED AND RAMAN SPECTRA OF TETRABROMOETHYLENE[1]

By F. E. Malherbe,[2] G. Allen,[3] and H. J. Bernstein

ABSTRACT

The infrared spectrum of liquid and dissolved tetrabromoethylene has been investigated from 3μ–36μ. The Raman spectrum has been obtained photographically in the liquid state and photoelectrically in solution and depolarizations measured. All of the fundamentals were observed except ν_4, ν_7, ν_{10}, and ν_{12}. The last two vibration frequencies are estimated by calculations from two different potential functions.

The infrared spectrum of dissolved and solid tetrabromoethylene has been obtained previously in the rock salt region of the spectrum (4). The Raman spectrum also has been obtained (9) in solution and as solid. Since it is now possible to investigate the infrared spectrum with CsBr optics and since the depolarizations of the Raman frequencies were not obtained previously reinvestigation of both spectra was considered to be worthwhile.

EXPERIMENTAL

The tetrabromoethylene used was the product of Matheson, Coleman and Bell Inc., East Rutherford, New Jersey, m.p. 56.5°, b.p. 227° at 760 mm. Hg. The infrared spectra were obtained in solution and as a molten liquid, with CsBr, KBr, NaCl, and LiF optics in a Perkin Elmer 12C Infrared spectrometer. To obtain the spectrum of the liquid a preheated sample was introduced into a liquid cell kept hot in a furnace arrangement (1).

The Raman spectra with depolarizations were obtained photographically (24 hr. exposure) with the instrument previously described (2) and also electronically recorded with a grating Raman spectrometer with photomultiplier detector.* The great advantage in having the electronically recorded spectrum is that the spectrum is obtained in about one-half hour during which the tetrabromoethylene does not undergo photochemical decomposition to any appreciable extent. The spectrum was recorded photoelectrically for a 30% tetrabromoethylene in carbon disulphide solution with slits of 5 cm^{-1}. Peak intensities were measured and corrected for the spectral sensitivity of the photomultiplier tube (10). The depolarizations were obtained in a manner described by Stamm (11). In order to obtain the Raman spectrum of the liquid, heated water (60°C.) was circulated through a jacket enclosing the Raman tube. The results are shown in Table I and Fig. 1.

DISCUSSION

Tetrabromoethylene belongs to the point group D_{2h} for which the symmetry types and selection rules may be found in Herzberg (5). In the Raman spec-

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa. Issued as N.R.C. No. 3118.
[2] *National Research Council Postdoctoral Research Fellow, 1950–1951.*
[3] *National Research Council Postdoctoral Research Fellow, 1952–1954.*
**This instrument was made by the White Development Co., Stamford, Connecticut.*

TABLE I

THE VIBRATIONAL SPECTRUM OF TETRABROMOETHYLENE

Raman				Infrared					Assignment
Solution[a]	Relative intensity and depolarization[b]	Solid[c]	Liquid[d]	Solution[e]	Liquid[f]	Solid[g]	Solid	Gas[i]	
144 (8)	(P)	154 (2)	144 ± 2						ν_3
211 (8)	21.5 (D)	187 (2)	208 ± 2						ν_6
266 (16)	100 (0.2)	267 (5)	265						ν_2
					366 w.				$\nu_{11} - \nu_2\ (B_{3u})$
					420 w.		[h]		$\nu_{11} - \nu_6\ (B_{2u})$
					463 w.				
463 (0)	3 (D)	478 (00)	464						ν_8
				498 w.	494 w.				709 − 211
				552 w.	552 w.	527 (10)			$\nu_9 - \nu_6\ (B_{3u})$
				631 s.	631 s.	630 (2)	630 s.	632 s.	ν_{11}
				694 w.	694 sh.		690 v.w.		
				708 w.	709 m.	716 (8)	711 w.	707 m.s.	847 − 144
				747 w.	745 w.				
				766 s.	767 s.	763 (10)	765 s.	770 v.s.	ν_9
				778 sh.	778 v.v.w.			784	$\nu_3 + \nu_{11}\ (B_{3u})$
				817 w.	817 w.		805 m.	810 v.w.	
				847 w.	847 m.	843 (10)	834 m.	852 s.	$\begin{cases} 709 + \nu_3 \\ \nu_6 + \nu_{11}\ (B_{3u}) \end{cases}$
				881 w.	883 w.	896 (6)			
886 (5)	9 (D)	884 (3)	880						ν_5
				904 v.	903 w.				$\nu_2 + \nu_9\ (B_{3u})$
	4 (P)		927						$2\nu_8$
				943 w.	944 w.	954 (6)		943 m.w.	
				974 w.	974 w.		[h]		$\begin{cases} 709 + \nu_2 \\ \nu_6 + \nu_9\ (B_{3u}) \end{cases}$
									$847 + \nu_3$
				998 w.	997 w.				
				1028 w.	1026 w.	1012 (8)		1028 m.	$\nu_2 + \nu_9\ (B_{3u})$
				1045 w.	1045 w.				$847 + \nu_6$
				1110 v.w.	1122 w.	1113 (6)			$847 + \nu_2$
						1296 (3)			

TABLE I (*Concluded*)

Raman				Infrared					Assignment
Solution[a]	Relative intensity and depolarization[b]	Solid[c]	Liquid[d]	Solution[e]	Liquid[f]	Solid[g]	Solid	Gas[i]	
1513 (3)	14 (0.7)	1517 (3)	1515						Fermi resonance of ν_1 and $2\nu_9$
					1527 w.				$\nu_5 + \nu_{11}$ (B_{3u})
1546 (4)	21 (0.5)	1546 (6)	1547						Fermi resonance of ν_1 and $2\nu_9$
					1733 w.				$847 + \nu_5$
					1756		[h]		
	5 (0.56)		1764						$2\nu_5$ (A_{1g})
					1788				
					2216				$709 + \nu_1$ (B_{3u})
					2265				$\nu_1 + \nu_9$ (B_{3u})
					2326				
					2394				$847 + \nu_1$ (B_{3u})

w = weak, m = medium, s = strong, v = very, sh = shoulder.

[a] *The results from reference (9).*

[b] *Tetrabromoethylene in carbon disulphide obtained with photoelectric instrument. The line at 266 cm.$^{-1}$ is taken to have intensity 100. The line at 144 cm.$^{-1}$ could not be measured because of grating ghost intensity.*

[c] *Reference (9).*

[d] *Obtained with photographic instrument in six hours.*

[e] *Carbon disulphide solution.*

[f] *Liquids were obtained in cells of different thickness so that the relative intensities have very little quantitative significance.*

[g] *The results from reference (4).*

[h] *Our results but these regions not investigated.*

[i] *Gas phase results obtained only in potassium bromide and sodium chloride regions.*

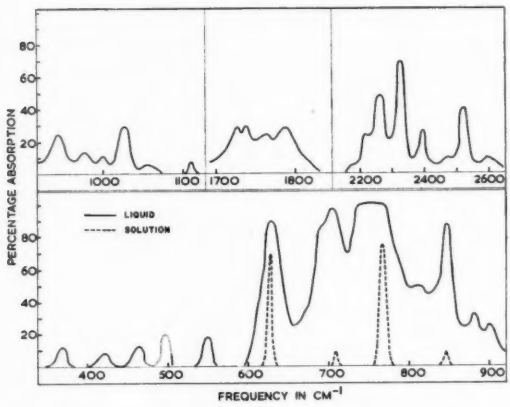

Fig. 1. The infrared spectrum of C_2Br_4; ———— liquid, – – – – – solution in CS_2.

trum there are six allowed fundamentals, three polarized Raman lines of type a_{1g}, two depolarized of type b_{1g}, and one depolarized of type b_{2g}. In the infrared spectrum there are five allowed fundamentals, two of type b_{2u}, two of type b_{3u}, and one of type b_{1u}. The torsion frequency of type a_{1u} is forbidden in both spectra. The mutual exclusion selection rule for molecules with a center of symmetry is well observed in the case of this molecule as can be seen from the table, no coincidences of frequencies being observed in the infrared and Raman spectra. Since the Raman lines at 1547, 1515, 267, and 144 cm.$^{-1}$ have been found to be polarized it is natural to select them as the a_{1g} vibrations describing approximately the C=C and C–Br stretching vibrations and the C–Br bending vibrations respectively. The doublet at 1547 and 1515 probably arises because of Fermi resonance (6) since the relative intensity of the two lines of the doublet changes from 1.5 in carbon disulphide solution to 2.1 in alcohol solution. It is probable that the energy levels of $2\nu_9$ and ν_1 (see Table I) are sufficiently perturbed in alcohol solution so that the resonance interaction is different, giving rise to intensity changes. Of the other Raman frequencies 885 and 211 cm.$^{-1}$ are chosen as fundamentals because of their intensity; 464 cm.$^{-1}$ is also chosen as the frequency of a fundamental since the vibration is out-of-plane and expected to be lower than either 925 or 1760 cm.$^{-1}$ which are taken as overtones. By analogy with the assignment in tetrachloroethylene and incidentally a confirmation** of this assignment of the b_{1g} frequencies in tetrachloroethylene, ν_5 is chosen as 885 cm.$^{-1}$ and ν_6 as 211 cm^{-1}. ν_8, the b_{2g} type frequency is then taken as 464 cm^{-1}.

In the infrared spectrum the dilute solution results show unequivocally that two of the fundamentals are at 767 cm.$^{-1}$ and 631 cm^{-1}. No other bands of appreciable intensity were observed down as far as 275 cm^{-1}. Our choice of

****It has been suggested that ν_5 in tetrachloroethylene is 512 cm.$^{-1}$ (P. Torkington, Trans. Faraday Soc. 45: 445. 1949) rather than 1024 cm.$^{-1}$ (H. J. Bernstein, J. Chem. Phys. 18: 478. 1950). The strong line at 884 cm.$^{-1}$ in tetrabromoethylene indicates that the higher of the two should be taken for ν_5 in tetrachloroethylene.**

fundamentals for this molecule differs from that of Guy and Lecomte (4) who made their assignment from solid spectra data only, and chose the bands at 767 cm.$^{-1}$ and 840 cm.$^{-1}$ as fundamentals. Our dilute solution data indicate that 840 cm.$^{-1}$ is too weak to be a fundamental. In order to decide whether 767 cm.$^{-1}$ was of type b_{2u} or b_{3u}, normal coordinate calculations were invoked using a potential function due to Morino, Kuchitsu, and Shimanouchi (8).

In reference (8) it is established that $\nu_5\nu_6 = 3.393\nu_9\nu_{10}$ if the CC and CBr internuclear distances are taken as 1.38Å and 1.91Å respectively and the BrCBr angle is 125°. Since ν_5 and ν_6 are reasonably well identified ν_{10} can be calculated if ν_9 is known. So that for

$$\nu_5 = 885 \text{ cm.}^{-1}, \nu_6 = 211 \text{ cm.}^{-1}, \text{ and } \nu_9 = 767 \text{ cm.}^{-1}, \nu_{10} = 72 \text{ cm.}^{-1},$$

whereas for $\nu_9 = 631$ cm.$^{-1}$, $\nu_{10} = 87$ cm.$^{-1}$;

thus ν_{10} is a very low lying frequency in the vicinity of 80 cm^{-1}.

Using $\nu_5 = 885$ cm.$^{-1}$, $\nu_6 = 211$ cm.$^{-1}$, and $\nu_9 = 767$ cm.$^{-1}$

and $H_{CCBr} = H_{BrCBr} = 0.11 \times 10^5$ dynes per cm.,

we find $K_2 = 2.91 \times 10^4$, $B = 2.10 \times 10^4$,

and $A - C = 2.6 \times 10^5$ dynes per cm.

Assuming further that all primed constants ≈ 0, we find

$F_{CBr} = 0.756 \times 10^5$, $H_{CCBr} = 1.06 \times 10^4$, and $K_{CBr} = 2.02 \times 10^5$ dynes per cm.

Now using $\nu_1 = 1547$ cm.$^{-1}$, $\nu_2 = 267$ cm.$^{-1}$, and $\nu_3 = 144$ cm.$^{-1}$,

we find $F_{BrBr} = 0.350 \times 10^5$ and $K_{CC} = 7.35 \times 10^5$ dynes per cm.

Using these constants in the expressions for the b_{3u} type frequency in reference (8) we calculate

$$\nu_{11} = 605 \text{ cm.}^{-1} \text{ and } \nu_{12} = 185 \text{ cm}^{-1}.$$

This is supporting evidence for the assignment of 767 cm.$^{-1}$ for ν_9 and 631 cm.$^{-1}$ for ν_{11}. If the calculation is performed with $\nu_9 = 631$ cm.$^{-1}$ instead of 767 cm.$^{-1}$ we find that the value obtained for K_{CC} is $< 4.0 \times 6^5$ dynes per cm. which seems physically unacceptable in view of the fact that most C=C force constants are $>7 \times 10^5$ dynes per cm. (7).

TABLE II

ASSIGNMENT FOR TETRABROMOETHYLENE

Type	Mode	Obs.	Calc.[b]	Calc.[c]
a_{1g}	ν_1	1547 / 1517 [a]		
	ν_2	267		
	ν_3	144		
a_{1u}	ν_4			
b_{1g}	ν_5	885		1650
	ν_6	211		206
b_{1u}	ν_7			
b_{2g}	ν_8	464		
b_{2u}	ν_9	767		
	ν_{10}		~80	133
b_{3u}	ν_{11}	631	605	
	ν_{12}		185	243

[a] *Fermi doublet.*
[b] *Calculated with potential function of reference (8).*
[c] *Calculated with potential function of reference (3).*

If the potential function of Bonner (3) is used, ν_{10} is calculated to be 133 cm.$^{-1}$ and ν_{12} is calculated to be 243 cm^{-1}. However, the constants*** used in this calculation yield values for ν_5 and ν_6 which are 1650 and 206 cm.$^{-1}$ respectively. The agreement with the observed value for ν_5 of 885 cm.$^{-1}$ is very poor.

The final assignment derived from our results is given then in Table II. The bands and frequencies listed in Table I have been tentatively interpreted on the basis of this assignment invoking binary and some ternary combination tones. The unassigned bands are all very weak and could possibly be interpreted on the basis of ternary combinations.

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***The force constants are found to be $K_1 = 6.99 \times 10^5$, $K + K_2 = 3.51 \times 10^5$, $H + \theta = 1.08 \times 10^5$, $\lambda = 0.04 \times 10^5$ dynes per cm. θ is assumed to be 0.16×10^5 dynes per cm. so $K - K_2 = 2.04 \times 10^5$ dynes per cm., and ν_{10} is found to be 133 cm^{-1}.

LIQUID-PHASE OXIDATION OF *p*-CYMENE: NATURE OF INTERMEDIATE HYDROPEROXIDES AND RELATIVE ACTIVITY OF THE ALKYL GROUPS[1]

By G. S. Serif[2], C. F. Hunt[3], and A. N. Bourns

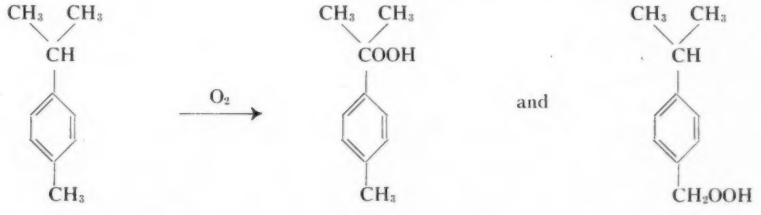
ABSTRACT

A study has been made of the liquid-phase oxidation of *p*-cymene with elemental oxygen using emulsion and photochemical procedures with the object of determining (*a*) the nature of the resulting hydroperoxides and their decomposition products, and (*b*) the relative activity of the methyl and isopropyl side chains.

The following compounds have been shown to be present in the emulsion oxidation product: 2-*p*-tolyl-2-propyl hydroperoxide, 2-*p*-tolyl-2-propanol, *p*-isopropylbenzyl alcohol, *p*-methylacetophenone, cumic acid, *p*-(α-hydroperoxyisopropyl) benzoic acid, *p*-(α-hydroxyisopropyl) benzoic acid, and *p*-acetylbenzoic acid. The two hydroperoxides have been isolated and characterized. By chromatographic separation of the carboxylic acids and fractional distillation of the alcohols formed by lithium aluminum hydride reduction of all other products, the relative susceptibility of the methyl and isopropyl groups to oxidative attack has been shown to be 1:4.

In the photochemical oxidation, hydroperoxide decomposition was very small and the product was shown to consist of 20% *p*-isopropylbenzyl hydroperoxide and 80% of 2-*p*-tolyl-2-propyl hydroperoxide. The relative extent of oxidative attack at the two positions was therefore identical in the two oxidations.

The preferred position of attack by elemental oxygen in the liquid-phase oxidation of alkyl benzenes has been shown to be the side-chain carbon directly attached to the aromatic ring, provided that this carbon is not quaternary (17). The initial products of such oxidations are hydroperoxides and, under appropriate conditions, these may be isolated and characterized. Included among the known hydroperoxides of this type are *p*-xylyl hydroperoxide (8), 1-phenylethyl hydroperoxide (8), and 2-phenyl-2-propyl hydroperoxide (9, 1). The hydrocarbon *p*-cymene, I, provides two centers for attack, the methyl carbon and the tertiary carbon of the isopropyl group, and two isomeric hydroperoxides, 2-*p*-tolyl-2-propyl hydroperoxide, II, and *p*-isopropylbenzyl hydroperoxide, III, may, therefore, be formed.



I II III

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Helberger, Rebay, and Fettback (6) studied the oxidation of *p*-cymene with oxygen in the presence of sunlight and isolated the sodium salt of the hydroperoxide by precipitation with aqueous sodium hydroxide. The hydroperoxide was considered to have structure III since cuminaldehyde could be isolated from the products of the decomposition of the salt in boiling water. Lorand (12), on the other hand, has reported that the sodium sulphide reduction of the hydroperoxide formed by oxidation of *p*-cymene with oxygen in the presence of aqueous alkali furnished a product consisting of 90% 2-*p*-tolyl-2-propanol and 10% *p*-methylacetophenone. The apparent absence of *p*-isopropylbenzyl alcohol in the reduction product would suggest that the tertiary hydroperoxide, II, was the only hydroperoxide formed by oxidation under these conditions.

The seemingly contradictory results obtained using the two oxidation methods are indeed surprising since current ideas concerning the mechanism of hydrocarbon oxidation (2) would strongly suggest that a product of similar composition should be obtained in each case. The present paper reports the results of a reinvestigation of the oxidation of *p*-cymene in which an effort has been made to determine quantitatively the composition of the total oxidation product formed using the two oxidation procedures. In addition to establishing the nature of the hydroperoxide product, this study has provided an accurate measure of the relative activity of the methyl and isopropyl groups toward oxidative attack.

Emulsion Oxidation

The oxidation in the presence of aqueous alkali was carried out using a procedure recently developed by Armstrong, Hall, and Quinn (1) for the preparation of tertiary hydroperoxides. Oxygen was passed into an emulsion of *p*-cymene and aqueous sodium carbonate in the presence of sodium stearate as the emulsifying agent and a small amount of cymyl hydroperoxide as the initiator. Oxidations were studied at 85 and 60°C. At the higher temperature the reaction was continued until the emulsion had broken, at which point the hydroperoxide concentration of the hydrocarbon had reached 40% by weight. At 60°C., however, the oxidation was very slow and the reaction was interrupted when a 19% hydroperoxide concentration had been attained.

On completion of an oxidation, the aqueous layer of the reaction product was separated and acidified, and the precipitated acids were then analyzed by a column partition chromatographic method. Four compounds were obtained: cumic acid, *p*-acetylbenzoic acid, *p*-(α-hydroxyisopropyl)benzoic acid, and a new hydroperoxide, *p*-(α-hydroperoxyisopropyl)benzoic acid. The structure of the latter was established by (*a*) neutralization equivalent, (b) peroxidic oxygen analysis, (*c*) reduction to the *p*-(α-hydroxyisopropyl)-benzoic acid, and (*d*) metal-catalyzed decomposition to the hydroxy acid and *p*-acetylbenzoic acid.

The organic layer was divided into two portions. *Aliquot I* was reduced with lithium aluminum hydride to furnish a product which was separated into two fractions by fractional distillation. The lower-boiling fraction was a

mixture of the tertiary and secondary alcohols, 2-*p*-tolyl-2-propanol and 1-*p*-tolylethanol, respectively, with the former predominating. The greater part of the tertiary alcohol resulted from the reduction of the tertiary hydroperoxide, II, although some was formed by decomposition of this hydroperoxide during the oxidation. The secondary alcohol was formed by reduction of *p*-methylacetophenone, a second decomposition product of the tertiary hydroperoxide. The smaller second fraction was the primary alcohol, *p*-isopropylbenzyl alcohol, formed from the primary hydroperoxide, III, by decomposition during the oxidation and by reduction with lithium aluminum hydride. The results of this fractionation, combined with those of the chromatographic analysis of the acids and the ketone analysis on Aliquot II, permitted the calculation of the relative extent of oxidative attack at the two available positions.

In order to obtain additional information on the composition of the oxidation product as well as to determine the nature of the hydroperoxide isolated by the sodium salt precipitation, the second portion of the organic layer, *Aliquot II*, was treated with a concentrated solution of sodium hydroxide. The insoluble hydroperoxide salt was filtered, the hydroperoxide liberated with carbon dioxide and reduced with lithium aluminum hydride to yield 2-*p*-tolyl-2-propanol in high yield. The absence of *p*-isopropylbenzyl alcohol in the reduction product established that the hydroperoxide actually *isolated* as the sodium salt from the products of the emulsion oxidation was the tertiary compound, II, uncontaminated with the primary isomer, III. The small organic layer of the filtrate from the sodium salt filtration was analyzed for its ketone (*p*-methylacetophenone) content and was then fractionated. A single fraction consisting of the tertiary alcohol, 2-*p*-tolyl-2-propanol plus a small amount of *p*-methylacetophenone was obtained.

The composition of the product from emulsion oxidations at 85 and 60°C., expressed as mole %, is shown in Table I.

TABLE I
COMPOSITION OF THE PRODUCTS OF THE EMULSION OXIDATION

Product	Mole %	
	85°C. Run	60°C. Run
2-*p*-Tolyl-2-propyl hydroperoxide	49.4	59.2
2-*p*-Tolyl-2-propanol	22.3	12.1
p-Isopropylbenzyl hydroperoxide plus *p*-isopropylbenzyl alcohol	7.5	10.3
p-Methylacetophenone	3.4	7.0
Cumic acid	11.7	9.6
p-(α-Hydroperoxyisopropyl)benzoic acid	2.9	1.2
p-(α-Hydroxyisopropyl)benzoic acid	1.7	0.4
p-Acetylbenzoic acid	1.1	0.2

Photochemical Oxidation

The procedure used in the so-called photochemical oxidation of *p*-cymene was similar to that described by Helberger *et al.* except that a mercury-vapor lamp was used as a source of illumination rather than sunlight. The reaction,

which was carried out at 60°C. only, was much slower than the emulsion oxidation and therefore was stopped when the hydroperoxide concentration was 5.5%.

Preliminary work had shown that carboxylic acids were present in the oxidation product to only a very small extent (less than 0.6% of the oxidized hydrocarbon) and consisted mainly of cumic acid. For this reason, the total reaction mixture was reduced directly with lithium aluminum hydride without making a preliminary alkaline extraction. Fractionation of the reduction product furnished the tertiary and primary alcohols, 2-*p*-tolyl-2-propanol and *p*-isopropylbenzyl alcohol, respectively. The total weight of the reduction product was almost identical with the weight expected from the reduction of the known amount of hydroperoxide in the oxidation mixture. Since such reductions are practically quantitative it was concluded that the photochemical oxidation product was almost entirely in the form of hydroperoxides. The composition of the product calculated on the basis that the total tertiary alcohol was formed by reduction of the tertiary hydroperoxide, II, and the primary alcohol by reduction of the primary hydroperoxide, III, was 79.5% II and 20.5% III.

Relative Activity of the Methyl and Isopropyl Groups

The extent of oxidative attack at the primary and tertiary α-carbon atoms *p*-cymene in the emulsion and photochemical oxidation is shown in Table II.

TABLE II
PER CENT ATTACK AT PRIMARY AND TERTIARY α-CARBON ATOMS

Position of attack	Emulsion oxidation		Photochemical oxidation
	85°C.	60°C.	60°C.
Primary carbon	22.0	20.8	20.5
Tertiary carbon	78.0	79.2	79.5

For the emulsion oxidation the per cent attack at the primary position has been calculated as the sum of the mole % of primary alcohol and hydroperoxide, the mole % of cumic acid, and one-half the mole % of the oxy-acids. Similarly, the extent of attack at the tertiary carbon has been calculated by summing the mole % of tertiary hydroperoxide, tertiary alcohol, and ketone, and one-half of the mole % of the oxy-acids. The per cent attack at the two positions in the photochemical oxidation has been based on the composition of the product as determined by reduction with lithium aluminum hydride and separation of the resulting alcohols.

DISCUSSION

The results presented in Table II indicate that within experimental error the *relative* activity of the methyl and isopropyl groups toward oxidative attack is the same in the emulsion and photochemical reactions. This, of course, is not surprising. The nature of the major proportion of the product

will be determined by the identity of the propagation steps and these are the same for oxidation under the two conditions, namely,

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot,$$

where R· is either the primary or tertiary cymyl radical and RO_2H is the corresponding hydroperoxide (2). Some product may be attributed to the initiation and termination steps of the oxidation, but since the reaction chains are probably fairly long, this will constitute a very minor proportion of the total. Furthermore, the relative activity of different radicals toward the primary and tertiary carbon atoms will be approximately the same regardless of their nature. Thus, some reaction chains in the emulsion oxidation may be initiated by RO· and HO· radicals formed by thermal decomposition of the hydroperoxide (18). The relative activity of these radicals towards the two reaction sites, however, should correspond closely to that of the RO_2· radicals acting in the propagation step.

It is of interest to compare the results of the present study with those reported by Kooyman (11) who obtained a measure of hydrocarbon activity in radical reactions by comparing the inhibiting action of different hydrocarbons in the propagation step of the peroxide-catalyzed addition of carbon tetrachloride to olefins. He has found that the ratio of the α-methylenic activity of the isopropyl group of cumene to that of the methyl group of toluene is 4.2:1 at 91.5°C. This corresponds fairly closely to the 3.5:1 ratio for the two groups obtained at 85°C. in the present study*.

As stated earlier, the isolation of cuminaldehyde from the products of the decomposition of the sodium salt of the hydroperoxide formed in a photochemical oxidation was considered by Helberger to characterize the hydroperoxide as the primary compound, III. This experimental result, confirmed in the present study, is not in conflict, however, with the fact that the oxidation product actually contains only 20% of III, the remainder being the tertiary hydroperoxide, II. It has been well established that primary hydroperoxides decompose very readily in the presence of alkali to form aldehydes. Hock and Lang (8), for example, obtained *p*-tolualdehyde in good yield by warming *p*-xylyl hydroperoxide with an equivalent of alkali for a few minutes. Tertiary hydroperoxides, on the other hand, are considerably more stable toward alkali, particularly when sufficient is present to convert the hydroperoxide to its salt. Thus, Kharasch (10) has shown that in the presence of excess alkali α-cumyl hydroperoxide is decomposed only to the extent of 70% at 90°C. in six hours and the main product is 2-phenyl-2-propanol. In the present investigation the treatment of the cymyl hydroperoxide salts for 15 min. with boiling water would be expected to completely decompose the

**Kooyman has also shown that whereas the activity of m-xylene is exactly twice that of toluene the activity of o- and p-xylene is significantly greater than twice. Because of this mutual interaction of groups in ortho and para positions the relative activity of the two alkyl groups of p-cymene, as determined in the present study, is not a true measure of the activity of methyl and isopropyl groups attached to the benzene ring. This could be determined, however, from a similar study of the oxidation of m-cymene.*

primary component to cuminaldehyde and partially decompose the tertiary component to the tertiary alcohol.

EXPERIMENTAL*

Purification of p-Cymene

Eastman Kodak "White Label" *p*-cymene was dried over Drierite and distilled over sodium through a 30 plate column. A mid-fraction, b.p. 62.5°C. (12 mm.), n_D^{20} 1.4908, was used in the oxidation studies.

Emulsion Oxidation

Apparatus

A train consisting of an activated charcoal tower, solid sodium hydroxide tower, back-splash trap, sulphuric acid trap, and glass wool tower was used to purify cylinder oxygen. Gas-flow rate was regulated by a needle valve and measured with a mercury flowmeter. The reaction vessel consisted of a three-neck five-liter flask provided with a fritted-glass gas dispersion tube, mercury-seal stirrer, thermometer, and condenser. The top of the condenser was connected through a dry-ice trap to a wet-test gasmeter.

Oxidation Procedure

The reaction vessel was charged with a reaction mixture of the following composition:

water	2000.0 gm.
p-cymene	340.0 gm.
stearic acid	3.0 gm.
sodium carbonate	27.0 gm.
cymyl hydroperoxide	0.4 gm.

The stirred mixture was brought to the desired temperature and the oxygen flow adjusted to seven liters per hour. The oxidation was followed using an iodometric procedure (7) for hydroperoxide analysis of samples periodically removed from the reaction flask. The reaction at 85°C. was stopped when the hydroperoxide content of the cymene had reached 40% by weight. This required 35.5 hr. The reaction at 60°C. was interrupted after 197 hr. at which time the hydroperoxide concentration was 19%. Two layers separated on cooling. The aqueous layer was separated and washed with petroleum ether (b.p. 30-60°C.), care being taken to retain the flocculent sodium stearate with the water. The ether washings were combined with the organic layer. The greater part of the ether was removed *in vacuo* and the residue divided into two aliquots for further treatment. The aqueous layer was acidified with dilute hydrochloric acid, the precipitated acids taken up in ethyl ether, the ether removed, and the acids separated by a chromatographic procedure.

Lithium Aluminum Hydride Reduction of Aliquot I

Aliquot I from each oxidation (three-quarters of the organic layer from the 85°C. reaction and one-half from the 60°C. reaction) was diluted with

**All melting and boiling points are corrected.*

500 ml. of ether and the solution added dropwise with stirring to a 25% excess of a 2 *N* ethereal solution of lithium aluminum hydride. The mixture was decomposed with water followed by sufficient 10% sulphuric acid to just barely dissolve the basic aluminum salts. The ether layer was separated and washed with 10% sodium bicarbonate. The ether was removed and the product fractionated in a 35 plate column (13) using benzhydrol as the chaser. Two fractions were obtained in addition to unreacted cymene. Fraction I, b.p. 105-106°C. (12 mm.) was a mixture of 2-*p*-tolyl-2-propanol and 1-*p*-tolylethanol. Fraction II, b.p. 125.5-126.5°C. (12 mm.) was *p*-isopropylbenzyl alcohol.* A phenylurethan derivative of this fraction melted at 62.0-62.5°C., reported 62.5°C. (14).

Treatment of Aliquot II

Aliquot II of each oxidation product was added slowly to twice its volume of an ice-cooled 25% solution of sodium hydroxide. The hydroperoxide salt separated in about two hours.** It was filtered rapidly using an ice cooled, fritted-glass funnel, washed with petroleum ether and dried. The salt was crushed to a fine powder, stirred with 150 ml. of petroleum ether, filtered and again dried. This product was suspended in water and the hydroperoxide liberated by passing in carbon dioxide until a pH of 8 had been reached. The hydroperoxide was taken up in petroleum ether and the ether removed *in vacuo*. The colorless oily residue analyzed for 98—99% cymyl hydroperoxide. It was diluted with ether and reduced with lithium aluminum hydride using the procedure already described. Fractionation of the reduction product in the 35 plate column using benzhydrol as the chaser furnished 2-*p*-tolyl-2-propanol, b.p. 105—106°C. (12 mm.), n_D^{20} 1.5174.† The yield was 93 and 91% based on the isolated hydroperoxide and 78 and 71% based on the hydroperoxide content of the original oxidation mixture for the 85 and 60°C. oxidations, respectively. There was no evidence of a *p*-isopropylbenzyl alcohol fraction boiling between the tertiary alcohol and the chaser.

The organic layer of the filtrate from the hydroperoxide salt filtration was separated and the petroleum ether distilled off. The residue was heated under reflux for three hours to decompose hydroperoxides and a sample was then removed for ketone analysis (16). The remainder on fractionation furnished a single fraction consisting mainly of 2-*p*-tolyl-2-propanol and *p*-methylacetophenone.‡ The primary alcohol, *p*-isopropylbenzyl alcohol, could not be isolated at this stage. Reduction with lithium aluminum hydride of the product of this distillation followed by a fractionation of the reduction product,

**Fractionation of a synthetic mixture of these alcohols demonstrated that the primary alcohol does not form an azeotrope with the other alcohol components.*

***Seeding of the alkaline mixture with a small amount of the hydroperoxide salt induced immediate precipitation. This method was used in the treatment of the 85°C. oxidation product and resulted in higher hydroperoxide recovery.*

†The slightly high refractive index of this product was attributed to the presence of a small amount of α, p-dimethylstyrene (n_D^{20} 1.5283) formed by dehydration of the alcohol. When the column was maintained at total reflux for a short period droplets of water appeared in the head and the refractive index of subsequent distillate increased.

‡The ketone was identified by means of its 2,4-dinitrophenylhydrazone, m.p. 259.8-260.6°C., which gave no melting point depression when mixed with an authentic sample of this derivative.

however, furnished a very small fraction boiling between the main product and the chaser. This was identified by its phenylurethan derivative as the primary alcohol.

Separation and Identification of the Carboxylic Acid Oxidation Products

The acids were separated by column partition chromatography using methanol on silicic acid as the stationary phase and benzene saturated with aqueous methanol as the mobile phase. The packing was prepared by grinding 150 gm. of Mallinckrodt A. R., 100 mesh, silicic acid with 200 ml. of methanol, 7.5 ml. of a 1% methanolic bromocresol green solution, and 2 ml. of 1 *N* ammonium hydroxide until a homogeneous powder was produced (15). The powder was slurried with 300 ml. of benzene and poured into 49 × 3.5 cm. (diam.) column. Benzene, equilibrated with 90% aqueous methanol, was forced through the column to remove excess indicator and, using this solvent as eluent, 0.5 gm. of cumic acid was then passed through to remove excess ammonium hydroxide. Elution with 'equilibrated' benzene of two grams of the acid oxidation product, placed on the column in 25 ml. of this solvent, produced four distinct bands. The eluent corresponding to each band was collected and the solvent removed *in vacuo* to give separated acids in a total recovery of 95—98%.

The first band emerging from the column comprised a mixture of cumic and stearic acids, which could not be separated adequately by the above described chromatographic procedure. Recrystallization of this mixture from aqueous ethanol, however, furnished a product which gave no melting point depression when mixed with an authentic sample of cumic acid and gave a neut. equiv. of 164.7, calc. 164.2. Since care had been taken to retain precipitated sodium stearate with the aqueous layer of the oxidation product a fairly accurate correction for the stearic acid present in the first band could be made.

The second acid, recrystallized from benzene–ethanol, was *p*-acetylbenzoic acid: m.p. found 209.2–209.8°C., reported (5) 208.6–209.4°C.; neut. equiv. found 168.2, calc. 164.2; phenylhydrazone m.p. found 234–235°C., reported 234°C.

The fourth acid to pass from the column was recrystallized from ethanol–benzene and identified as *p*-(α-hydroxyisopropyl)benzoic acid: m.p. found 159.2—159.6°C., reported (4) 156°C.; neut. equiv. found 180.5, calc. 180.2.

The third acid after recrystallization from benzene–ethanol gave a melting point of 151.5—151.8°C. Its neut. equiv. and peroxidic oxygen content agreed with the calculated values for *p*-(α-hydroperoxyisopropyl)benzoic acid: neut. equiv. 196.9, calc. 196.2; peroxidic oxygen found 16.34, 16.28, calc. 16.31%.

The hydroperoxy acid was further identified by sodium sulphide reduction to *p*-(α-hydroxyisopropyl)benzoic acid. The acid, 0.085 gm., was refluxed overnight with 10 ml. of water, 0.05 gm. of sodium carbonate and 0.10 gm. sodium sulphide hydrate. The product was acidified and the precipitated acids separated chromatographically by the method already described.

There was obtained 0.069 gm. (88%) of *p*-(α-hydroxyisopropyl)benzoic acid and 0.003 gm. (4%) of *p*-acetylbenzoic acid.

Finally, the hydroperoxy acid was decomposed in the presence of cobalt ion. The acid, 0.150 gm., was refluxed for three hours with 45 ml. of benzene and six drops of cobalt napthenate solution (Nuodex Cobalt 6%). The product was taken up in 10% sodium carbonate, and the acids precipitated with dilute hydrochloric acid. Using crystallization and chromatographic procedures, 0.059 gm. (43%) of *p*-(α-hydroxyisopropyl)benzoic acid and 0.0465 gm. (37%) of *p*-acetylbenzoic acid was obtained.

Preparation and Properties of 2-p-Tolyl-2-propyl Hydroperoxide, II

The sodium salt of the hydroperoxide, isolated from the products of a separate 85°C. oxidation in the manner already described, was converted to the free hydroperoxide by treatment with carbon dioxide and then reprecipitated. The salt (97.4% pure) was treated with carbon dioxide and the liberated hydroperoxide extracted with petroleum ether. Removal of the ether left a colorless oily liquid which analyzed for 98.9% hydroperoxide. Distillation *in vacuo* furnished a colorless liquid: b.p. 88—91°C. (1 mm.); n_D^{20} 1.5207; d_4^{25} 1.0403; peroxidic oxygen found 19.04, 19.12%, calc. 19.25%. On the basis of the results obtained from the reduction of the hydroperoxide described above, this product was considered to be essentially pure tertiary hydroperoxide, II.

Photochemical Oxidation

Apparatus and Procedure

The apparatus was identical with that used for the emulsion oxidations except that the reactor was a two-liter flask surrounded by a box lined with aluminum foil. The box was fitted with a 100 watt bulb connected to a Variac to provide a variable heat source and across an open end was aligned an 18 in. long quartz d-c. mercury-vapor lamp. The flask was charged with 850 gm. of *p*-cymene, the temperature raised to 60°C., and the oxygen flow started and adjusted to seven liters per hour. After 118 hr., a hydroperoxide concentration of 5.5% by weight had been reached and the reaction was then stopped.

Lithium Aluminum Hydride Reduction

The total oxidation product was reduced with lithium aluminum hydride using the procedure already described. The reduction product was fractionally distilled using benzhydrol as the chaser. Two fractions were obtained in addition to unchanged *p*-cymene. Fraction 1, b.p. 105—106°C. (12 mm.), n_D^{20} 1.5172, wt. 34.1 gm. was 2-*p*-tolyl-2-propanol, and Fraction 2, b.p. 125.0—126.5°C. (12 mm.) n_D^{20} 1.5204, wt. 8.8 gm. was *p*-isopropylbenzyl alcohol. The total weight of 42.9 gm. compared with a theoretical yield of 42.4 gm. based on the hydroperoxide content of the oxidation product.

ACKNOWLEDGMENTS

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THE EFFECT OF PHYSICAL ADSORPTION ON THE ELECTRICAL RESISTANCE OF ACTIVE CARBON[1]

By W. W. Smeltzer[2] and R. McIntosh[3]

ABSTRACT

The change of the electrical resistance of active carbon rods due to the reversible adsorption of vapors is described. The effects of six saturated hydrocarbons and ethyl chloride were studied. An interesting regularity in the results obtained with the hydrocarbons was found, namely that the extent of the resistance change at a given temperature and volume adsorbed is proportional to the number of carbon atoms in the adsorbate molecule. The alteration of the electrical conductivity of the active carbon by the physically adsorbed vapors and the adsorption isotherms are not modified by small quantities of chemisorbed oxygen. Ethyl chloride exhibits a more complex behavior than the hydrocarbons. It is argued that the resistance measurements may be utilized to support the viewpoint that physically adsorbed saturated hydrocarbon molecules tend to lie flat on the adsorbent surface. Several possible explanations of the findings are examined and proved to be inadequate.

INTRODUCTION

In an earlier publication McIntosh, Haines, and Benson (12) reported variations of the electrical resistance of active carbon rods when vapors, usually considered to be physically adsorbed, were taken up by the adsorbent. The extent and direction of the resistance changes at a fixed temperature were found to be dependent upon the chemical nature of the adsorbate molecules. The effect of physical adsorption on the change of the linear dimension of the rods was also examined (9). It was concluded that the mechanical alteration of contact resistances between the granules forming the rod could not be the explanation of the phenomena, because no correlation between dimensional and resistance variations was found. An example leading to this conclusion was the comparison of effects caused by butane and ethyl chloride. Both of these adsorbates bring about a marked increase in the length of the rod. The dimensional change per unit quantity of adsorbed vapor is greatest near saturation of the surface. In this region a negligible change of resistance was observed in the case of butane, whereas a marked change was found with ethyl chloride. On the basis of such evidence it was suggested that the adsorbates alter either the mobility or the number of conducting electrons in the semiconductor (12).

Somewhat similar observations have been reported for other systems. Baxter (3) has explained the effect of adsorbed water on the electrical resistance of wool fibers by assuming that the water molecules act as impurity donors. Conduction was postulated to occur by transfer of electrons from one adsorbed water molecule to another. The conductivity was assumed to depend upon the width and height of the potential barrier and thus increased with moisture

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content. More recently the examination of very thin metallic films (13, 14), which exhibit a temperature coefficient of resistance characteristic of semiconductors, has revealed that their resistance is diminished by adsorbed gases. The effect was found to be reversible at pressures below 10^{-4} mm. The resistance alteration was explained by assuming a lowering of potential barriers between the metallic aggregates of the films by adsorbed gases.

Further experiments have been completed with active carbon because adsorption is readily measured, and because this adsorbent should be suitable for study if the effect is dependent upon a large surface to volume ratio. The obvious difficulty is that the conduction mechanism in polycrystalline carbons is not well understood. Mrowzowski (15) has discussed this subject in some detail. In this investigation the adsorption isotherms and the concomitant resistance changes have been determined at several temperatures. Because hydrocarbon vapors produced the simplest type of change, the investigation was largely directed to a study of the effect of saturated hydrocarbons on a carefully evacuated rod, or on one which, after evacuation, was allowed to chemisorb oxygen. Certain regularities in the results obtained with these adsorbates are apparent, but no adequate explanation of the effects has been achieved. The polar adsorbate ethyl chloride was also examined, and the complexity of the phenomena is well illustrated by the results obtained.

EXPERIMENTAL

The procedures and methods of measurement were identical with those described in the earlier publication (12). Four rods were used in investigating the temperature variation of resistance. The lengths between the potential measuring electrodes of rods 4, 6, 8, 9 were 7.1, 6.9, 8.1, and 7.0 cm. respectively. Rod 4 was evacuated to a reproducible resistance at 120°C., rods 6 and 8 at 160°C., and rod 9 at 240°C. Two rods were utilized for adsorption experiments but as the same characteristic effects were exhibited by each rod, only experiments are recorded in which rod 8 was used. A tubular air oven was employed for the resistance measurements as a function of temperature. It was also used as the thermostat at temperatures above 30°C. The temperature in the oven was uniform to within 0.2°C. over a length greater than the length of the glass envelopes containing the rods, and was controlled manually to within ±0.1°C. whenever equilibrium measurements were taken. Temperatures were measured by means of a thermocouple fastened to the glass envelope. Adsorption isotherms at temperatures lower than 30°C. were determined in a large Dewar vessel thermostat. The bath temperature was established by means of a refrigerator coil and an automatically controlled heater. Fluctuations of the bath temperature did not exceed ±0.05°C. Adequate precautions were taken to eliminate any conduction paths between electrodes or to ground.

RESULTS

Variation of Electrical Resistance with Temperature

The temperature variation of resistance of the active carbon rods is shown in Fig. 1, and obeys the relation $\log_{10} R = A - BT$, where R is the resistance

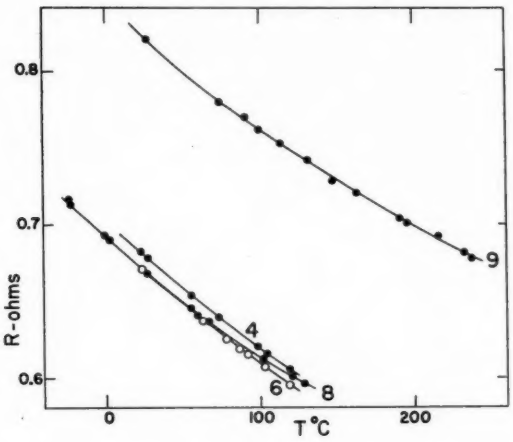

FIG. 1. Variation with temperature of electrical resistance of active carbon rods 4, 6, 8, and 9.

in ohms, A and B are constants, which was reported previously (12). It may be interpreted according to the views put forward by Mrowzowski when discussing baked carbons (15). For baked carbons of similar specific resistance to the active carbon rods, and prepared by baking at about 750°C., Mrowzowski suggested a minimal energy gap between valence and conduction bands of 0.2 ev. This value is supported by reference to measurements of infrared absorption. Thermoelectric effects revealed that an essentially constant number of conduction electrons exists in the temperature range wherein the resistance of the baked carbons was determined, and these two facts were interpreted as showing that the variation of resistance is due to diminished scattering. The specific resistances of the active carbon rods 4, 6, 8, and 9, calculated using a cross sectional diameter of 8 mm., are 0.05, 0.05, 0.04, and 0.06 ohm cm., respectively. The rods were prepared by the zinc chloride process of activation involving carbonization at about 750°C. On the basis of these similarities, the variation with temperature of the resistance of the active carbon rods may be accounted for by a decreased scattering of electrons in the polycrystalline structure with increasing temperature. The large electrical conductivity is presumed to arise from the presence of a large and nearly constant number of excess electrons in the conduction band. The electrons are assumed to be associated with the peripheral carbon atoms, and their unsaturated valence bonds at the surface discontinuities of the solid. They are mobile and contribute to the conductivity. A decrease of resistance caused by the presence of adsorbate molecules would thus necessarily be due to a change in the mobility or scattering of the electrons. Such a postulate would be extremely difficult to formulate quantitatively, and we have adopted other descriptions of the nature of the carbon surface in the attempts made to explain the results observed with the physically adsorbed vapors.

Effect of Hydrocarbons

The resistance effects of six hydrocarbon adsorbates were studied. The vapors used were methane, ethane, propane, *n*-butane, cyclopropane, and isobutane. All the hydrocarbons were investigated over a range of temperature except methane, for which the temperature of −21.3°C. was employed so that the amount adsorbed would be appreciable. The results obtained for

TABLE I
DATA FOR CYCLOPROPANE ON ROD 8

Temperature, °C.	Volume adsorbed, cc. vapor N.T.P.	Equilibrium pressure, mm. Hg	Resistance, ohms
−22.0	0.00	0.00	0.7128
	34.9	0.13	0.7086
	72.2	0.61	0.7055
	117	1.69	0.7023
	162	4.76	0.6996
	220	6.90	0.6967
	272	12.0	0.6943
	330	23.2	0.6917
	387	44.0	0.6895
	445	81.9	0.6879
	502	132	0.6867
	570	227	0.6856
−5.6	0.00	0.00	0.6967
	40.4	0.53	0.6925
	80.7	2.07	0.6894
	134	6.30	0.6858
	189	14.9	0.6829
	249	24.8	0.6800
	307	44.4	0.6777
	364	82.7	0.6754
	415	144	0.6739
	473	251	0.6727
	537	403	0.6716
	604	603	0.6707
12.4	0.00	0.00	0.6797
	38.5	1.27	0.6759
	76.8	5.40	0.6728
	121	13.2	0.6702
	171	25.6	0.6675
	222	46.8	0.6650
	272	76.1	0.6629
	329	136	0.6609
	388	253	0.6588
	442	430	0.6577
	485	609	0.6568
27.9	0.00	0.00	0.6662
	37.3	3.02	0.6628
	79.6	12.2	0.6596
	127	29.0	0.6568
	176	55.1	0.6544
	222	91.8	0.6523
	276	160	0.6501
	333	284	0.6482
	378	450	0.6468
	419	666	0.6459
	379	448	0.6470
	306	211	0.6494

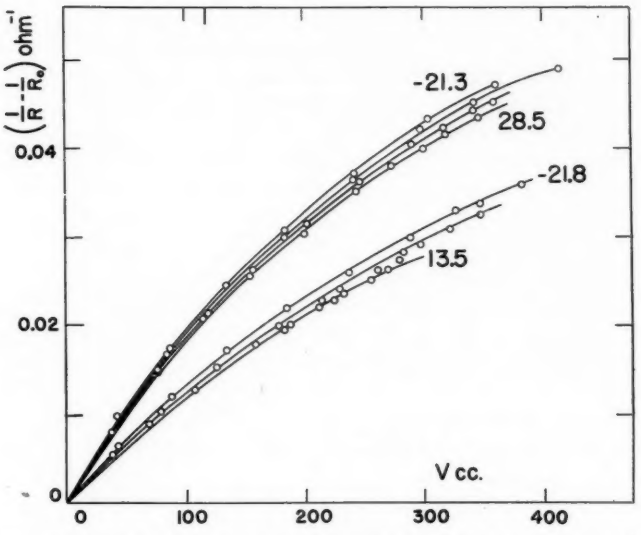

FIG. 2. Conductivity changes versus volumes adsorbed for hydrocarbons, rod 8.
Ethane adsorption—lower curves
Propane adsorption—upper curves

cyclopropane on rod 8 at four temperatures are recorded in Table I. The resistance effects of ethane and propane are illustrated in Fig. 2.

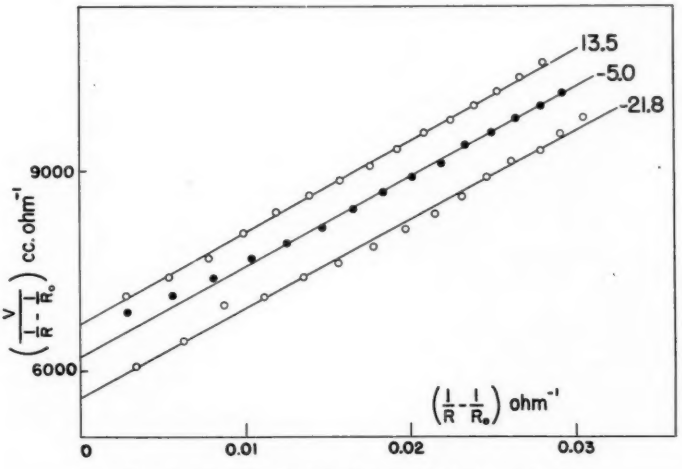

FIG. 3. Representation of the analytical equation

$$V \Big/ \left(\frac{1}{R}-\frac{1}{R_0}\right) = C + D\left(\frac{1}{R}-\frac{1}{R_0}\right)$$

for ethane adsorption on carbon rod 8.

The results may be summarized as follows. A decrease in the resistance is observed on the adsorption of the hydrocarbons, the magnitude of which increases with increasing amount of adsorbate on the surface, and appears to approach a limit asymptotically. The effect of the hydrocarbons increases with decreasing temperature.

Certain common features are apparent for all the hydrocarbons. The variation of resistance as a function of quantity adsorbed may be expressed empirically by the equation

$$V \Big/ \left(\frac{1}{R} - \frac{1}{R_0}\right) = C + D\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

where V designates the volume of adsorbed vapor in cc. at N.T.P., R is the measured resistance of the rod, R_0 is the resistance of the evacuated rod, and C and D are constants at the particular temperature. The range of validity of this relation, illustrated in Fig. 3 for ethane at three temperatures, was up to two thirds of the maximum volume adsorbed. From the intercepts C of this type of plot, the values of the tangents to the curves of Fig. 2 relating change of conductivity to volume adsorbed at zero adsorption were readily obtained. The values of these limiting tangents and these values, divided by N, the number of carbon atoms in the adsorbate molecules, are recorded in Table II.

TABLE II

LIMITING TANGENTS, k_1, TO CURVES FOR ALTERATION OF CONDUCTIVITY VERSUS ADSORBED VOLUME ON ROD 8

Temp., °C.	$k_1 \times 10^4$, ohm^{-1} per cc.	$(k_1/N) \times 10^4$, ohm^{-1} per cc.
Methane		
−21.8	1.05	1.05
Ethane		
−21.8	1.79	0.90
−5.0	1.62	0.81
+13.5	1.49	0.75
Propane		
−21.3	2.89	0.96
−5.0	2.75	0. 2
13.5	2.65	0.88
28.5	2.56	0.85
Cyclopropane		
−22.0	2.92	0.97
−5.6	2.79	0.93
12.4	2.73	0.91
27.9	2.65	0.88
n-Butane		
−22.0	3.66	0.92
1.4	3.57	0.89
26.2	3.31	0.83
54.3	3.05	0.76
Isobutane		
−21.3	3.85	0.96
3.0	3.75	0.94
27.9	3.55	0.89

It is evident that the values of the tangents divided by N are common for all the hydrocarbons at a given temperature within about 10%. On the basis of this finding it was shown that either the conductivity or resistance alterations for all the hydrocarbons can be represented by a common curve as in Fig. 4,

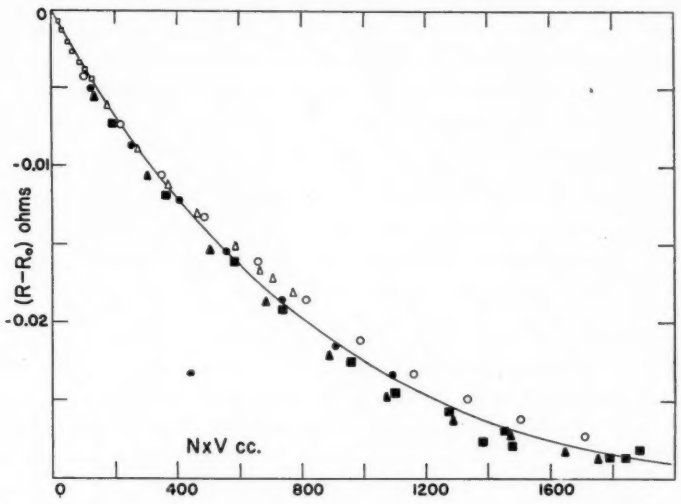

FIG. 4. Resistance changes versus adsorbed volumes of hydrocarbons multiplied by factor N. Temp. −21.5°C.

□ Methane ○ Cyclopropane ■ *n*-Butane
△ Ethane ● Propane ▲ Isobutane

where the change of resistance is plotted against the product of the volume adsorbed and the number of carbon atoms in the adsorbate molecules using data obtained at -21.5 ± 0.5°C. The generalization attempted by this treatment is clearly not exact, but departures from it are comparatively small, and do not correlate immediately with the structure of the adsorbate molecule. As some of the discrepancies may be due to experimental error, it seems best to regard the observation as a good first approximation. Some discussion of the results is useful at this point.

It could be postulated that the change of resistance is directly proportional to the amount of hydrocarbon which is adsorbed in the first layer, and that the decreasing extent of the effect per unit quantity adsorbed may be accounted for by a greater proportion of the adsorbate being adsorbed into higher layers as the quantity on the surface is increased. If this view is adopted, the quantity of vapor required to complete the monolayer may be evaluated by an extrapolation of the tangent to the curve relating resistance change to volume adsorbed at zero adsorption, until it meets the limit of the change of resistance. The volume of vapor adsorbed corresponding to this point would then give the quantity required to complete the monolayer. The value deduced for *n*-butane by this method was found to be 165 cc. The B.E.T. (7) determination

of the monolayer volume, on the other hand, was 321 cc. This method of obtaining the monolayer volume is generally accepted (8, 10). However, Pierce, Wiley, and Smith (17) contest this view, and argue that the generally accepted values of surface areas of active carbons are much too large. In the case of porous glass, Amberg and McIntosh (1) found that the surface area determined by the B.E.T. method agreed with an estimate made on the basis of capillary condensation theory. Because of this controversy, a final decision cannot presently be reached, but it may be noted that the electrical effect might be employed to measure the monolayer volume for active carbons if the gas adsorption method based on the B.E.T. equation is inadequate. For the present the view is adopted that adsorption of the vapors is occurring into the first layer, since the B.E.T. C value is large, and that some other explanation of the experimental results is required. The varying effect of the conductivity alteration with increasing coverage cannot be due to a difference of orientation of the adsorbed molecules on the surface. This view is untenable because methane, a spherical molecule, shows the same characteristic behavior as the other molecules. The electrical data suggest that the hydrocarbon molecules lie with their major axis in the plane of the adsorbent surface, because the electrical effect is found to be proportional to the number of carbon atoms in the adsorbate molecules. This conclusion has been arrived at on the evidence of heats of adsorption (4, 6) and surface area evaluations (16) with hydrocarbon vapors. The isosteric heats of adsorption of the hydrocarbons are shown in Fig. 5 to an accuracy of about ±300 cal./mole. The branched chain methyl

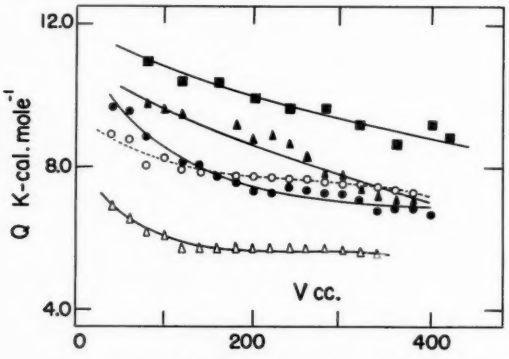

FIG. 5. Isosteric heats of adsorption of hydrocarbons.

△ Ethane ● Propane ▲ Isobutane
○ Cyclopropane ■ *n*-Butane

group of the isobutane molecule should be at a greater distance from the surface than the rest of the molecule if the molecule lies flat on the adsorbing surface. The isosteric heat of adsorption for isobutane, which is intermediate between that of *n*-butane and the heats of adsorption of the propanes, tends to substantiate this viewpoint. As shown in Fig. 4, however, the resistance variations caused by the two butanes are essentially the same. Consequently,

the resistance effect is much less sensitive to the value of the equilibrium distance from the surface than is the heat of adsorption.

It becomes necessary to account for the form of the conductivity versus volume adsorbed curves by other means if the conclusions are accepted that the molecules tend to lie flat on the surface of the solid and are adsorbed into the first layer. It is possible that the number of electrons in the conduction band of the semiconductor is altered by the adsorbate. It was postulated that the electrons of the free valencies at the surface discontinuity were bound to the surface carbon atoms in contradiction to the concept put forward by Mrowzowski. Since the resistance effect was found to be proportional to the number of methyl or methylene groups in the adsorbate molecule, it was further assumed that the surface atoms may form complexes with these groups. The complexes then act as donors of conduction electrons. That is, the reaction,

$$\text{surface complex} \rightleftarrows \text{ionized surface complex} + \text{free electron},$$

is assumed. The total number of complexed surface atoms was taken as the number of adsorbed molecules multiplied by the number, N, of carbon atoms per molecule. The conductivity $1/R_0$ of the evacuated carbon rod was regarded as proportional to the number and mobility of electronic carriers. The conductivity change is directly proportional to the increased number of carriers if it is assumed that their mobility is not altered when adsorbate is *in situ*. The equilibrium constant of the assumed reaction may then be expressed in terms of the measured resistance and volume of adsorbed vapor by means of the usual type of equilibrium equation. Such a treatment is valid if the semiconductor is nondegenerate (18). The resulting relation is identical in form to the empirical equation (1) given above. However, its use leads to absurd results, since the proportionality constant between number of additional carriers created by the adsorption process and the conductivity is negative in value. The same analytical form may also be obtained, if, in conjunction with the reaction suggested, the postulate is made that the electrons originally present in the conduction band of the solid do not enter into the equilibrium reaction. This treatment is also not valid, since it leads to the result that the number of conduction electrons produced by the reaction is in excess of 10^{21} for a solid containing about 5×10^{22} carbon atoms. Classical equilibrium equations would thus not be applicable for such a large number of electrons.

Experiments with Chemisorbed Oxygen

The resistance of carbon rod 8 was altered by the chemisorption of oxygen to determine whether the number of electrons originally in the conduction band of the solid modifies the effect of the hydrocarbon adsorbates. The surface of the active carbon was therefore exposed to oxygen at 600 mm. pressure at three temperatures, 12.4°C., 120°C., and 130°C. After each exposure the rod was evacuated at room temperature until a 'stick' vacuum was obtained. An adsorption isotherm using cyclopropane was determined at 12.4°C. after each evacuation. In addition one isotherm using ethane was determined after the final treatment of the rod with oxygen. Both of these

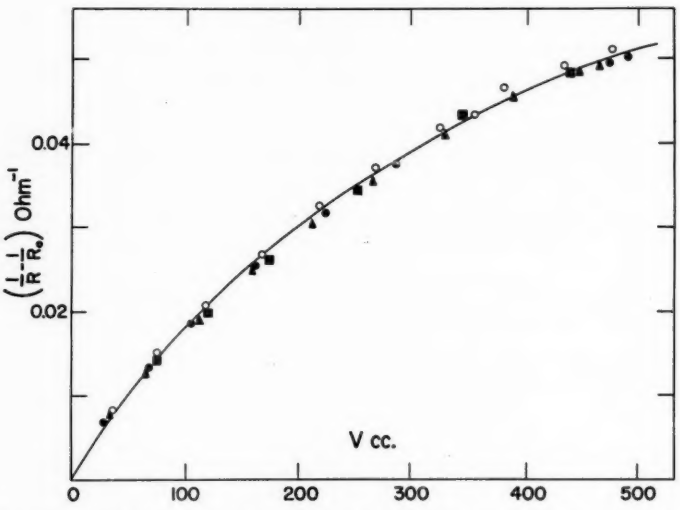

FIG. 6. Conductivity changes versus volumes adsorbed cyclopropane on rod 8 with oxygen at 12.4°C.

○ Bare rod

Resistance alteration with oxygen

■ 0.0028 ohm

● 0.0223 ohm

▲ 0.0520 ohm.

adsorbates gave the usual conductivity effect. It is shown in Fig. 6 that within experimental accuracy the conductivity effect is not modified although successive changes of the original resistance of the rod to the extent of 0.0028, 0.0233, and 0.0320 ohm were obtained by the treatment with oxygen. It is reasonable to postulate that the electronegative oxygen causes an increase of resistance because it is chemisorbed on peripheral carbon atoms which act as donors, with a resulting localization of conduction electrons. A reduction of the number of mobile electrons to an extent of about 7% does not, therefore, alter the effect of the hydrocarbon. This observation supported the treatment of the equilibrium process in which only the electronic carriers formed by the adsorption of the vapor were taken into account. However, as the assumed reaction does not rationalize the observed results, the effect of oxygen must be regarded merely as an additional fact which a postulated mechanism must explain. It is believed that peripheral foreign atoms such as oxygen form high resistance barriers in baked carbons (15). It might be assumed that some of these barriers are sufficiently opaque to reduce the number of conduction paths in a porous solid. If one attempts to explain the conductivity effect of hydrocarbons on such a premise, it would follow that its magnitude should be different for the bare rod and the oxygenated one. The experimental results however lead to the conclusion that this effect of chemisorbed oxygen is negligible.

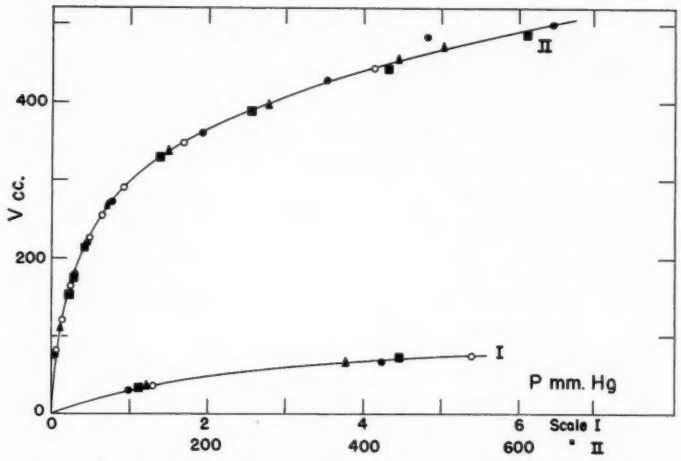

FIG. 7. Adsorption isotherms of cyclopropane on rod 8 at 12.4°C. (points designated as in Fig. 6).

The adsorption isotherms of cyclopropane and ethane were unaltered by the small addition of chemisorbed oxygen to the active carbon. The graphical representation of the cyclopropane results in Fig. 7 illustrates this. All the adsorbates displayed Type I adsorption isotherms. The equation

[2] $$\log (V/P) = A - BV$$

where A and B are constants for a specified temperature gave the best analytical representation of the adsorption isotherm at surface coverages greater than 100 cc. of adsorbed vapor.

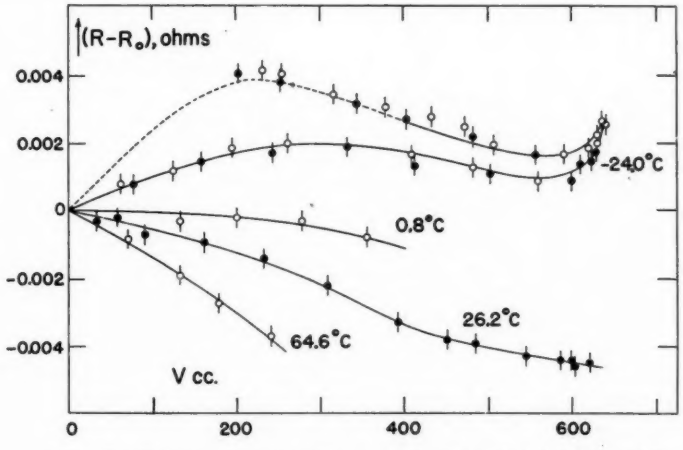

FIG. 8. Resistance versus volumes adsorbed for ethyl chloride, rod 8.

Effect of Ethyl Chloride

The alteration of resistance due to ethyl chloride is shown in Fig. 8. The direction and magnitude of this alteration is dependent upon the volume of adsorbed vapor and the temperature. The resistance is diminished by this adsorbate at 64.6°C. whereas at −24.0°C. the resistance increases appreciably on adsorption of vapor. Again, such behavior is not specific to a given rod as similar results were obtained with rod No. 4. The abrupt increase of the change of resistance near saturation of the surface referred to in the introduction is well illustrated. The resistance variation was not reversible, although the adsorption isotherm was. The latter statement could not be demonstrated in the low pressure region; that is, below the pressure corresponding with the volumes indicated on the solid curve of Fig. 8. Volumes indicated on the dotted portion of the curve were taken from the adsorption isotherm and a knowledge of the equilibrium pressures. It was demonstrated that prolonged pumping at the temperature of the isotherm caused the resistance to return to its original (R_0) value. On readsorption after partial desorption, the resistance followed the desorption branch. The findings are too complex to permit interpretation. The hysteresis of the resistance change may be due to a small number of ethyl chloride molecules, not easily removed in desorption, bound interstitially in the expanded graphitic crystallites. It is known that bromine is bound in this manner in graphite (11). It should be noted, however, that the resistance alteration, at a specified temperature, is characteristic of the adsorbate, and that the temperature coefficient of the effect may vary from one adsorbate to adsorbate.

GENERAL DISCUSSION

The attempts made to account for the observed phenomena have involved the postulate that the presence of physically adsorbed molecules on the surface of the carbon semiconductor alters the number of conduction electrons rather than their mobility. Direct evidence of this is lacking, but could perhaps be obtained by measurements of the thermoelectric effect of the semiconductor in gaseous environments. Bardeen (2) has introduced the concept of surface states on the free surface of a semiconductor. A total surface dipole exists because of a space charge region which extends from the surface into the bulk of the solid. An alteration of the number of electrons trapped in surface states can be brought about by the application of an external electric field. The alteration of the contact potential between an N-type germanium semiconductor and platinum, in the presence of polar vapors, has been treated quantitatively on the basis of the theory of surface states by Brittain and Bardeen (5). Stuetzer (19) has shown that the electrical conductivity of an N-type germanium semiconductor is increased if a polar liquid such as nitrobenzene is present at the surface. It is suggested that excess holes are formed in the valence band owing to the repelling field of the oriented polar molecules. In the case of active carbon, donor traps at the surface appear indicated because peripheral carbon atoms are the source of electrons in the conduction band. The conductivity effect due to physically adsorbed vapors may thus be due to

shifts of the equilibrium among electrons in surface states and in the conductivity and valence bands of the solid. This effect would be especially noted for active carbon because of its large surface to volume ratio. A demonstration that the effects are due to changing number of carriers is not possible by resistance measurements alone.

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ION EXCHANGE SEPARATION OF AMMONIUM AND GUANIDINE SALTS[1]

By Marcel Bertrand and J. L. Myers

ABSTRACT

A procedure for the determination of mixtures of guanidine and ammonium salts which employs an ion exchange separation prior to analysis is described. Details of the ion exchange and the results obtained with synthetic mixtures are presented. The recommended procedure permits estimation of guanidine in the presence of up to ten times its weight of ammonium salt.

INTRODUCTION

The ion exchange mechanism has attracted widespread attention in recent years and the method of separation described herein is an application of this principle.

In analysis of guanidine by picrate precipitation erroneous results are obtained in the presence of large concentrations of ammonium ions (1). If the ammonium ion could be removed by ion exchange, it would be possible to determine mixtures of guanidine and ammonium salts irrespective of their composition.

The behavior of guanidine and ammonium ions on the cation resin exchanger Nalcite was studied and it was established that these ions could be quantitatively separated by this means.

(A) DISTRIBUTION CURVE

After considerable experimentation, a pyrex glass tube, 3.50 sq. cm. in cross sectional area and 35 cm. in length, was selected. It contained 25.3 gm. of oven dried Nalcite HCR (Canadian trade name for Dowex 50). The Nalcite rested on a sintered glass filter of medium porosity and filled the tube to a height of 14.2 cm., giving a bed volume of 50 ml.

Nalcite resin of regular size was placed in the tube and prepared for use by backwashing with water until the liquid above the resin was clear. This procedure is necessary to prevent subsequent clogging of the glass filter by minute resin particles. To ensure complete conversion to the hydrogen form, the resin was then washed with approximately normal hydrochloric acid until the effluent and influent concentrations were the same.

The exchanger was then saturated with approximately 1.7 *N* sulphuric acid which was prepared by diluting 50 ml. of concentrated sulphuric acid to one liter. One gram samples containing a mixture of ammonium sulphate and guanidine nitrate were dissolved in 10 ml. of 1.7 *N* sulphuric acid. After introduction of the sample and before starting the elution, the column was drained until the level of liquid was one millimeter above the level of the exchanger. The column was then eluted with 1.7 *N* sulphuric acid at the rate of 6.5 ml./

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min. Elutions were performed at room temperature. Fifty-milliliter fractions of eluate were collected in volumetric flasks. Under these conditions the ammonium sulphate appeared in the first 15 fractions and guanidine in the 30 following.

Determination of Ammonia

The eluted fractions containing ammonium ions were analyzed by the micro-Kjeldahl method (3). An aliquot of 20 ml. was transferred to a Parnas and Wagner micro-Kjeldahl apparatus, 15 ml. of 30% sodium hydroxide solution were added, and the ammonia was steam distilled into 5 ml. of 2% boric acid solution for three minutes. The solution was then titrated with 0.01 *N* hydrochloric acid, using four drops of 5 : 1 bromocresol green/methyl red mixed indicator.

Determination of Guanidine

Guanidine was analyzed by Sullivan's colorimetric method (4), using a Fisher Electrophotometer AC model with a 525 mμ green filter. One milliliter of aliquot of the eluate was transferred into a 50 ml. volumetric flask and 2 ml. of freshly prepared 1% solution of 1,2-naphthoquinone-4-sodium sulphonate were added, followed by 0.5 ml. of 4 *N* sodium hydroxide. This solution was allowed to stand in a boiling water bath for two minutes; then cooled under running water. Three milliliters of 2.5% urea solution were added, followed by 1 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid (density 1.42). The solution was mixed and diluted to the mark with 50–50 ethanol–water solution. The contents were transferred to the cell and compared to distilled water by means of the electrophotometer.

The above method offered the following advantages:

(*a*) Rapidity with which analyses can be performed.

(*b*) High accuracy attained at the low concentrations of guanidine encountered in this work.

The calibration curve obtained with the Sullivan's method using a standard solution of guanidine nitrate in 1.7 normal sulphuric acid solution is shown

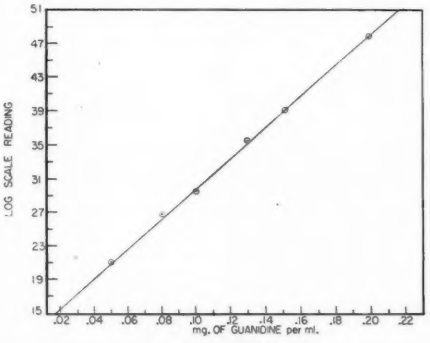

FIG. 1. Calibration curve for colorimetric analysis of guanidine with 1,2-naphthoquinone-4-sodium sulphonate.

in Fig. 1. This curve illustrates the accuracy and reproducibility achieved by strict adherence to the specified procedure.

Results

A typical graph for the separation and recovery of ammonium and guanidine salts (Fig. 2) shows that a good, clear separation was attained. This curve is

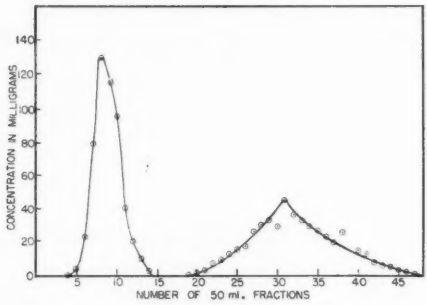

FIG. 2. Elution of ammonium and guanidine salts. Conditions: Column, 3.50 sq. cm. × 14.2 cm.
Exchanger, 25.3 gm. of HCR Nalcite (oven-dried basis).
Elutrient solution, 1.7 N H_2SO_4.
Flow rate, 6.5 ml./min.
Temperature, 27°C.

obtained by plotting the concentration of the ammonium or guanidine salts in milligrams in the eluate as ordinate and the number of 50 ml. fractions of eluate as abscissa.

From this curve, it is apparent that the ammonium ions are less strongly absorbed and are eluted in the first 15 fractions. Several fractions are free of cations and then the more strongly bound guanidine ions are slowly eluted in the next 30 fractions.

(B) ANALYTICAL PROCEDURE

Although the study of the distribution curve showed that guanidine and ammonium ions could be separated on a cation exchange column the procedure was too long and tedious for analytical use. Accordingly a more rapid procedure was investigated.

A pyrex glass tube 3.14 sq. cm. in cross sectional area and 42 cm. long was selected. It contained 45.1 gm. of oven dried Nalcite which filled the tube to a height of 28 cm. giving a bed volume of 85 ml. Nalcite resin was conditioned in the same manner as in Section (*A*) and converted to the hydrogen form. Elutions were performed at room temperature, first with approximately 1 N and later with 6 N hydrochloric acid.

One gram samples containing a mixture of ammonium sulphate and guanidine nitrate were dissolved in 10 ml. of 1 N hydrochloric acid. The exchanger was previously saturated with normal hydrochloric acid. After introduction of the sample, the column was drained until the level of the liquid was one millimeter above the level of the exchanger. The ammonium ion was then

eluted with 1000 ml. of 1 *N* hydrochloric acid at a rate of 6–6.5 ml./min. The eluate was collected in a 1000 ml. volumetric flask and adjusted to the mark with distilled water at 20°C. The elution acid was replaced by 6 *N* hydrochloric acid and an additional 300 ml. were collected at the same rate of flow.

Determination of Ammonia

The analysis of ammonia was carried out in triplicate on suitable aliquots, using the procedure described in Section (*A*).

Determination of Guanidine

The 300 ml. eluate was evaporated to near dryness on a steam plate to remove the hydrochloric acid. To assure complete evaporation of the hydrochloric acid, 25 ml. of distilled water was added and the mixture re-evaporated to dryness. The residue was taken up with 25 ml. of distilled water and the solution heated until concentrated to 15 ml. The determination was then completed using the calcium picrate method (2).

Results

It was found that the use of different acid concentrations in (*B*) gave a more rapid separation since the two salts were separated and eluted in 1300 ml. of eluate instead of 2500 ml. The time was reduced to $3\frac{1}{2}$ hr. compared to $6\frac{1}{2}$ hr. in the previous experiment. Hydrochloric acid was used instead of sulphuric acid in the final procedure because of its greater ease of evaporation from the solution.

It was found that with 6 *N* hydrochloric acid, all guanidine was eluted from the column in six fractions instead of the 30 fractions obtained with 1.7 *N* sulphuric acid (see Table I). Typical data of the separation and recovery of ammonium and guanidine are given in Table II.

TABLE I
ELUTION OF GUANIDINE WITH 6 *N* HYDROCHLORIC ACID IN SIX FRACTIONS

Guanidine nitrate		
Added, gm.	Found, gm.	Recovery, %
0.5060	0.5049	99.8
0.5010	0.5002	99.8
0.5025	0.5012	99.7

TABLE II
SEPARATION OF AMMONIUM AND GUANIDINE SALT

Ammonium sulphate eluted with 1000 ml. of *N* HCl			Guanidine nitrate eluted with 6 × 50 ml. of 6 *N* HCl		
Added, gm.	Found, gm.	Recovery, %	Added, gm.	Found, gm.	Recovery, %
0.5013	0.4988	99.5	0.5017	0.4942	98.5
0.5023	0.4987	99.3	0.5107	0.5035	98.6

Fainer and Myers (2) claim that their calcium picrate method for the determination of guanidine tolerates large amounts of ammonium salts as impurities. The results in Table III show that this is true up to a ratio of 1 : 2 of ammonium to guanidine salt. Above this ratio accurate results are not obtainable.

TABLE III

DETERMINATION OF GUANIDINE IN PRESENCE OF AMMONIUM IONS USING THE CALCIUM PICRATE METHOD

Ratio* of mixture	Guanidine nitrate			Ammonium sulphate added, gm.
	Added, gm.	Found, gm.	Recovery, %	
1 : 1	0.5022	0.4994	99.4	0.5034
1 : 1	0.5007	0.4986	99.6	0.5012
1 : 2	0.3548	0.3556	100.2	0.6674
1 : 5	0.1549	0.4451	287.3	0.8878
1 : 7	0.1215	0.4122	339.2	0.8864
1 : 10	0.0912	0.2184	239.5	0.9104

**Approximate ratio of guanidine to ammonium salts.*

By the use of the ion exchange column, even a 1 : 10 ratio mixture can be analyzed. Table IV shows the results of a series of experiments with ratios similar to those in Table III.

TABLE IV

ANALYSIS OF MIXTURES OF GUANIDINE AND AMMONIUM SALTS BY ION EXCHANGE COLUMN

Ratio* of mixture	Guanidine nitrate by calcium picrate method			Ammonium sulphate by Kjeldahl distillation		
	Added, gm.	Found, gm.	Recovery, %	Added, gm.	Found, gm.	Recovery, %
1 : 1	0.5017	0.4942	98.5	0.5013	0.4988	99.5
1 : 2	0.3570	0.3488	97.7	0.6655	0.6560	98.6
1 : 5	0.1525	0.1448	95.0	0.8692	0.8524	98.1
1 : 7	0.1217	0.1176	96.6	0.8833	0.8865	100.3
1 : 10	0.0890	0.0837	94.0	0.9165	0.9175	100.1

**Approximate ratio of guanidine to ammonium salts.*

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NOTES

SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
VIII. DEUTERIUM SUBSTITUTION PRODUCTS OF ETHYL ACETATE[1]

By B. Nolin

The deuterium labelling technique was used recently in the study of the infrared absorption spectrum of pentanone-3 (5). To extend this method of investigation to ethyl acetate, several deuterium substitution products were required in which one or more of the hydrogen containing groups are completely deuterated. This paper deals with the synthesis of seven deuterated ethyl acetates. The results of the spectroscopic investigation will be reported in a subsequent publication.

Several routes to the desired compounds were considered. On the 10–25 millimole scale, the reaction between the silver salt of acetic acid and ethyl iodide (4) proved the most suitable, because the corresponding deuterated materials could be obtained in high purity and no by-products are formed in the reaction. The esters were thus prepared by the following scheme:

$$RCOOAg + R'I \longrightarrow RCOOR' + AgI,$$

where R = CH_3 or CD_3, and R′ = CH_3CH_2,CH_3CD_2, CD_3CH_2, or CD_3CD_2.

Deuterated silver acetate of high isotropic purity was prepared as described in a previous paper (6); the isotopic determination was carried out by mass spectrometer analysis of samples of deuterated methyl bromide prepared by brominative degradation of the silver salt essentially as reported in the above-mentioned paper. This analytical procedure is now recommended for the accurate determination of the deuterium content of the alkyl groups of lower fatty acids, whatever the isotopic purity may be. For such an analysis, no special purification of the silver salt is required. The decarboxylation is readily carried out in a straight sealed tube with less than a gram of material and the deuterated bromide is merely freed from carbon dioxide and excess bromine by passing the reaction product through Ascarite.

The deuterated ethyl iodides were obtained from the corresponding bromides by an extension and modification of Spindler's method (7) which consists in treating an alkyl bromide with calcium iodide in a sealed tube. According to this author, who investigated bromides higher than ethyl, the conversion was incomplete. In the present work the conversion of ethyl bromide was carried nearly to completion by a second treatment with calcium iodide.

Ethyl-2-d_3 bromide was prepared through this sequence of reactions: alkylation of ethyl malonate with methyl-d_3 bromide (6) essentially as reported in (9) for the preparation of the normal compound, hydrolysis of the reaction product to methyl-d_3 malonic acid, decarboxylation of the dibasic acid to propionic-3-d_3 acid, and finally brominative decarboxylation of silver propionate-3-d_3 as described in a previous paper for silver acetate-d_3 (6). Höle-

[1]*Issued as N.R.C. No. 3108.*

mann and Clusius had prepared propionic-3-d_3 acid but by a different method (2).

Ethyl-1-d_2 bromide was prepared by the brominative degradation of silver propionate-2-d_2. The preparation of propionic acid labelled in the methylene group (95.0 atom % deuterium) had been reported (2).

EXPERIMENTAL*

Deuterated Ethyl Acetates

The preparation of ethyl-d_5 acetate-d_3 is given as a typical procedure. Ethyl-d_5 iodide** (4.4 gm.) was transferred through a vacuum line to a small flask containing silver acetate-d_3*** (4.6 gm.). The flask was removed from the manifold, attached to a reflux condenser, and heated overnight at 95°C. The volatile material was separated from the inorganic residue and found by mass spectrometer analysis to contain a small amount of unreacted ethyl-d_5 iodide. The mixture was therefore treated as before with fresh silver acetate-d_3 (2.3 gm.). The ester, now free from ethyl iodide, was treated three times with small amounts of phosphoric anhydride, that is until the latter was not discolored within five minutes. The material was degassed in the usual way and a very small fraction was removed. The bulk had a practically constant vapor pressure at 0°C. Yield, 2.0 gm., 75%.

The refractive index, vapor pressure at 20°C., and isotopic purity expressed in deuterium atoms per molecule of ethyl-d_5 acetate-d_3 are listed in Table I,

TABLE I
PHYSICAL PROPERTIES OF NORMAL AND DEUTERATED ETHYL ACETATES

Compound	D atoms per molecule		n_D^{20}	Vapor pressure (mm., 20°C.)
	Found	Required		
$CH_3COOCH_2CH_3$	—	—	1.3723*	72.9**
$CH_3COOCD_2CH_3$	1.98	2	1.3718	74.2
$CH_3COOCH_2CD_3$	2.97	3	1.3716	74.0
$CD_3COOCH_2CH_3$	2.97	3	1.3712	74.8
$CH_3COOCD_2CD_3$	4.97	5	1.3710	75.0
$CD_3COOCD_2CH_3$	4.97	5	1.3707	75.3
$CD_3COOCH_2CD_3$	5.92	6	1.3704	75.9
$CD_3COOCD_2CD_3$	7.94	8	1.3700	76.3

*Literature (8), 1.37233.
**Literature (10), 72.8 mm.

together with those of six partially deuterated ethyl acetates and normal ethyl acetate prepared in the same way. The isotopic purity of the deuterated esters was determined by mass spectrometry and corresponded to 98.8–99.4 atom % deuterium. The vapor pressures were measured with an apparatus similar to that described by Booth and Swinehart (1); they are higher than

*All mass spectrometer analyses are corrected for C_{13}.
**The isotopic purity of this iodide, ethyl-d_3 iodide, and ethyl-d_2 iodide corresponded to 99.2 atom % deuterium or more.
***99.3 atom % deuterium.

the vapor pressure of normal ethyl acetate, which is raised on complete deuteration by 1.0 and 3.4 mm. at 0°C. and 20°C. respectively. The refractive index of ethyl acetate is lowered on deuteration, the average difference being 0.0003 unit per carbon–deuterium bond.

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The author is very grateful to Dr. L. C. Leitch who has initiated the present series of papers on the synthesis of organic deuterium compounds and in whose section this work has been done. Thanks are also due to Miss F. Gauthier and Miss J. Fuller for the mass spectrometer analyses.

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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
IX. BISTRIDEUTEROMETHYL MERCURY*

By E. E. Bevege, R. Renaud, and L. C. Leitch

Although several methods have been reported for the preparation of dimethyl mercury (5) which is widely used in photochemical work as a source of methyl radicals, none of them is suitable for the synthesis of the deuterated analogue where economy of deuterated reactants is of paramount importance. It appeared to us that bistrideuteromethyl mercury would be readily prepared by the method employed by Emeléus and Haszeldine (1) for the synthesis of organo fluorine compounds. The methyl-d_3 iodide required in the present work was prepared as recently reported by Nolin and one of us (3, 4). When it was heated in a sealed tube for several days at 125°C. with cadmium amalgam a 75% yield of bistrideuteromethyl mercury was obtained. Its deuterium content was essentially the same as that of the methyl-d_3 iodide. The vapor pressure of deuterated dimethyl mercury, measured as described in an earlier paper (2), is 17.9 mm. at 0°C. compared with 17.4 mm. for the normal compound.

The synthesis described in detail below could probably be used in preparing deuterated diethyl mercury from the corresponding deuterated ethyl iodide.

Bistrideuteromethyl Mercury

Cadmium amalgam was prepared by shaking 13.0 gm. of cadmium turnings and 20 ml. of redistilled mercury in a bottle. The amalgam was poured into a

*Issued as N.R.C. No. 3117.

tube (12 in. × 1 in.) with a constriction and a joint for attaching it to a vacuum line. Methyl-d_3 iodide (12.5 gm.) was distilled into the evacuated tube which was then carefully sealed off at the constriction. The reactants were heated for a day at 100°C. and three days at 125°C. There was no pressure in the cold tube when it was opened. The volatile material was distilled off on the vacuum line into a trap and fractionally distilled at 0°C. into other traps on the line. After collecting 0.1 ml. (vapor pressure 19.5 mm. at 0°C.), the main fraction (2.2 ml.) had a constant vapor pressure of 17.9 mm. at 0°C. Analysis by mass spectrometry indicated the compound contained no methyl-d_3 iodide.

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THE PHOTOGRAPHIC RECORDING OF PAPER CHROMATOGRAMS OF CARBOHYDRATES AND A NEW SPRAY REAGENT*

BY G. L. KILGOUR AND G. G. S. DUTTON

The standard method of spraying paper chromatograms of sugars with various reagents to give colored spots (1) is in many cases satisfactory but the method has certain disadvantages. The most important one is that the colored spots produced are not stable indefinitely and hence such chromatograms are not satisfactory for reference purposes. It has been noted that the colored spots absorb strongly in the ultraviolet and we have been able to utilize this fact in making photographic copies of chromatograms.

A paper chromatogram is run in the normal way and after removal from the tank or cabinet is thoroughly air-dried to remove solvent, sprayed with any of the recommended reagents (1), and again dried. When dry, the chromatogram is laid on the emulsion side of a piece of photographic paper** and the two sheets are then stretched over a gently curved surface. This is important in order to get maximum contact between the chromatogram and the photographic paper, otherwise the spots will be very diffuse. The photographic paper is now exposed by holding a small ultraviolet source, e.g. a Mineralight, about twelve inches above the paper for one or two seconds. The photographic paper is then processed in the normal way.

*This work was undertaken while one of us (G.L.K.) was the holder of a Powell River Company Limited Scholarship, and we also wish to acknowledge financial assistance from the National Research Council.

**We have used Kodabromide A5 obtainable in rolls of 200 ft. and 4¼ in. wide from Air Photo Supply Corp., 555 East Tremont Avenue, New York 57, N.Y.

This method has the advantage that the chromatogram is unharmed and as many copies as may be required can readily be made from the same chromatogram. In addition, the photographic print gives a clear indication of the size and exact shape of the spots which facilitates R_f measurements and permits of rough quantitative estimations. Further, very often spots will show up under ultraviolet illumination, and hence on the photographic copy, which would not have been rendered visible by the ordinary spraying technique and inspection in visible light. This applies particularly to uronic and biuronic acids.

In this connection we have noted that all spray reagents do not give the same response with different sugars. In an attempt to find a spray not suffering from such a defect a new reagent was created, aniline hydrogen malonate. This was found to be decidedly superior to any other reagent used for the simple sugars, especially when dissolved in glacial acetic acid (2%) instead of butanol. This spray reacts equally with pentoses and hexoses giving pink and green colors respectively. However, it is not satisfactory for uronic acids and we found that aniline trichloroacetate was the best spray for general work (1), although the malonate reagent causes less discoloration of the paper.

It would seem wise to draw attention to the inadvisability of relying only on one spray reagent in any initial investigation of a carbohydrate material by means of paper chromatography especially if use is not made of ultraviolet light photographs.

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CORRECTION

Page 284. For "2-methylamino-2-oxazolidine" in the paper "Reaction of methylamine with 1-nitroso-2-nitramino-2-imidazoline" please read, "2-methylamino-2-oxazoline".

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